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THE SULPHIDES OF COPPER.

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INTRODUCTION.

This paper is a part of a general physico-chemical investigation of the copper sulphide and copper-iron sulphide minerals which at the present time is being carried on in this laboratory, in collaboration with a number of geologists under the leadership of Professor L. C. Graton, of Harvard University. Some time ago Professor Graton, with the support of many of the American copper companies, undertook a comprehensive study of the problems of the secondary enrichment of copper sulphide ores. A thorough geological investigation of most of the important copper sulphide deposits in North America was to be carried on in connection with a microscopic study of the ores at the Harvard Mining School. The desirability of chemical research on these problems was evident, and in view of the fact that considerable experience had been accumulated in this laboratory on the mineral sulphides, Professor Graton entered into an arrangement with the Carnegie Institution under which the Geophysical Laboratory was to undertake a simultaneous investigation of the conditions of formation and alteration of the more important minerals of the copper sulphide deposits, working as far as possible in coöperation with the geologists. This coöperative investigation has been in progress now for over two years, and though the difficulties involved in it are not to be minimized, the chemical researches, at least, have profited greatly from this collaboration.

Valuable geologic data have been placed at our disposal, helpful suggestions and criticisms have been received, and misconceptions have been avoided. On the material side we have been able to get many mineral specimens, often accompanied by field data which have greatly facilitated our studies.

The processes of ore deposition and alteration are undoubtedly chemical and it is equally certain that many, if not most of them, can be reproduced in the laboratory. To accomplish this, however, we need not only the aid of reliable field observations but a complete chemical and physical knowledge of the substances involved,—the composition and reactions of the minerals, the *general* conditions of their formation, the temperature ranges of their stability and their physical constants. Many of these data have never been determined and others need to be revised before the problems of ore deposition and alteration can be successfully elucidated.

Of the minerals to which studies of this nature are being devoted in this laboratory, the present paper deals with the two simple copper sulphide minerals, the cuprous sulphide, chalcocite, and the cupric sulphide, covellite. Of all the copper minerals chalcocite is the most abundant and economically the most important, and while covellite is not abundant it is very widely distributed and doubtless significant in the processes of ore deposition and secondary enrichment.

CUPROUS SULPHIDE (CHALCOCITE).

FORMATION, MELTING TEMPERATURE AND SPECIFIC GRAVITY.

Cuprous sulphide is dimorphous. In nature, as far as known, faceted crystals occur in the orthorhombic form, while synthetic cuprous sulphide made at elevated temperatures crystallizes in the isometric form. When pure it is of lead gray color and possesses a metallic lustre.

Cuprous sulphide is never obtained in pure condition by fusion of copper and sulphur, but always contains an excess of sulphur, as will be discussed later. When cupric sulphide is heated in a current of hydrogen for a short time, cuprous sulphide of approx-

imate purity is obtained, and this reaction is the basis for one of the analytical methods for the determination of copper. However, Pickering[1] and Wegscheider[2] state that hydrogen reduces cuprous sulphide at 600°, and the method is therefore rather uncertain.

We prepared pure crystalline cuprous sulphide by heating fused copper sulphide preparations in a vacuum furnace up to the melting point. The apparatus employed[3] consisted of a glazed porcelain tube 50 cm. in length, 3 cm. outside diameter and closed at one end. This tube stood vertically in an electric resistance furnace. The upper open end of the tube was closed with a brass plug which had an opening for the thermoelement and a side connection to the pump. The brass plug was cemented to the porcelain tube air-tight with "Khotinsky" cement, as was also the thermoelement in the brass plug. The cemented joints were of course kept cool by suitable means. In the porcelain cylinder was placed a graphite crucible with cover (3.5 cm. in length, 1.8 cm. inside diameter) containing the substance. In the latter was set the thermoelement protected by a porcelain jacket. We used graphite crucibles, as porcelain crucibles broke almost invariably.

After cooling, the graphite was removed from the melt and the products were analyzed. They proved to be practically pure cuprous sulphide, as seen from Table I.

TABLE I.

ANALYSES OF SYNTHETIC CUPROUS SULPHIDES.

No.	Found.			Cal. for Cu_2S.
	1	2	3	
Cu	79.76	79.80	79.74	79.85
S	20.25	20.12	—	20.15
Total	100.01	99.92	—	100.00

The same apparatus which was used in the preparation of cuprous sulphide served also for the determination of its melting point. The data obtained are given in Table II.

[1] Fittich's Jahresber., 1881, p. 261.

[2] Monatshefte 14, 315, 1893.

[3] See Allen, Crenshaw and Johnston, *Am. J. Sci.* (4), 33, 169, 1912.

TABLE II.

MELTING AND FREEZING TEMPERATURES OF CUPROUS SULPHIDE IN VACUO.

No.	Thermoelement.	Melting Temperature.		Freezing Temperature.	
		Mv.	°C.	Mv.	°C.
1	I	11076	1129.5	11060	1128
2	A	11070	1131	—	—
3	B	11078	1130	11042	1126

As seen from the table a slight undercooling takes place, but the melting point is sharp and may be regarded as $1130° \pm 1°$. Some of our preparations were heated as high as 1200° but no dissociation of cuprous sulphide could be observed at this temperature.[4] The melting temperature of synthetic cuprous sulphide as determined by previous observers is given in Table III.

TABLE III.

MELTING TEMPERATURE OF SYNTHETIC CUPROUS SULPHIDE GIVEN BY OTHER OBSERVERS.

Le Chatelier[5]	1100°
Bodlander and Idaszewsky[6]	1091°
Heyn and Bauer[7]	1127°
Röntgen[8]	1085°
Friedrich[9]	$1135° \pm 10°$
Bornemann[10]	$1100° \pm 4°$
Truthe[11]	1114°

Heyn and Bauer and also Friedrich melted their preparation under a layer of charcoal to protect it from oxidation. Heyn

[4] Specks of metallic copper were sometimes found in the melt. Continuous heating of such a preparation in vacuo at 1200°, however, did not increase the amount of copper and it therefore could not be due to dissociation of cuprous sulphide at this temperature. It probably was due to the reduction of cuprous sulphide by some gases occluded in the crucible or evolved by the glaze of the porcelain.

[5] *Bull. Soc. Chim.*, 47, 300 (1887).

[6] *Z. f. Elektrochemie*, 11, 161 (1905).

[7] *Metallurgie*, 3, 73 (1906).

[8] *Metallurgie*, 3, 479 (1906).

[9] *Metallurgie*, 4, 671 (1907); 5, 52 (1908).

[10] *Metallurgie*, 6, 619 (1906).

[11] Dissertation, Göttingen, 1912.

and Bauer state that their synthetic copper sulphide contained 99.71 per cent. Cu_2S. Friedrich's analysis showed 79.56 per cent. Cu and 20.48 per cent. S. The data given by both of these investigators are in fair agreement with ours. The other observers probably did not have pure cuprous sulphide and their values are all too low.

Determinations of the specific gravity of our synthetic cuprous sulphide preparations were made and compared with the specific gravity of pure natural chalcocite. (For analyses of the latter see Table XI.) The experimental data obtained are given in the table below.

TABLE IV.

SPECIFIC GRAVITIES OF PURE NATURAL AND SYNTHETIC CHALCOCITE AT 25°.

Source of Chalcocite.	Mineral 25° / Water 25°	Mineral 25° / Water 4°	Calculated.
New London mine, Md.	5.800	5.783	
Bristol mine, Conn.	5.797	5.781	
Butte, Mont.	5.791	5.774	
Synthetic cuprous sulphide (1)	5.801	5.784	
Synthetic cuprous sulphide (2)	5.802	5.785	

As seen from this table the specific gravity of synthetic and pure natural cuprous sulphide is the same. The values given in the text-books range from 5.5 to 5.8. The highest value given, as is usually the case with this constant, is much nearer the correct one.

COPPER SULPHIDES OF VARIABLE COMPOSITION (SOLID SOLUTIONS).

OBSERVATIONS OF OTHERS ON THE COMPOSITION OF THESE PRODUCTS.

It has been mentioned above, that when copper and sulphur are fused together the product always contains more sulphur than cuprous sulphide. The sulphur in such products can not be driven off by ordinary heating even at high temperatures. This was discovered by Hittorff[11a] as early as 1851 and he explained it by assuming that these products contained some cupric sulphide.

[11a] *Pogg. Ann.*, 84 (1851).

Recently his observations have been confirmed by Schubert,[12] Friedrich[12a] and Wasjuchnova.[13] The last-named author thought, as did Hittorff, that these substances contained some cupric sulphide, possibly forming a solid solution. It seemed to us of interest to investigate this more closely.

VARIATION IN COMPOSITION WITH TEMPERATURE WHEN HEATED IN HYDROGEN SULPHIDE.

The variation in the composition of copper sulphide when heated at varying temperature in an atmosphere of hydrogen sulphide was determined by a method previously used in this laboratory for the investigation of pyrrhotite, i. e., the crucible was suspended in the upper portion of an upright porcelain tube which was heated by an electric resistance furnace, the lower portion of the tube being kept cool so that when equilibrium was reached the crucible could be chilled by lowering. In the present case the chilling was facilitated by surrounding the lower end of the tube with ice water.

Since ordinary hydrogen sulphide always contains free hydrogen,[13a] due to the fact that the ferrous sulphide from which it is derived always contains metallic iron, another method of preparation was resorted to. The method of Divers and Shimidzu,[14] which consists in the decomposition of a solution of magnesium hydrosulphide by heating it to 60–90°, was found to be adequate. The gas was dried before passing it into the apparatus.

The products melted in hydrogen sulphide and then suddenly cooled by lowering the crucible to the bottom of the tube crystallized and had the composition given in Table V.

The influence of temperature on the composition of copper sulphide heated in hydrogen sulphide was determined by holding the sulphide in a powdered condition at a given temperature for a sufficient time and then chilling. The temperature was kept con-

[12] Dissertation, Dresden, 1910.
[12a] *Loc. cit.*
[13] Dissertation, Berlin, 1909.
[13a] In our analyses as much as 10 per cent. was found.
[14] *J. Chem. Soc.*, 699 (1884).

TABLE V.

THE COMPOSITION OF COPPER SULPHIDE WHEN MELTED AND QUICKLY COOLED IN HYDROGEN SULPHIDE.

No.	% Cu.	% S.	Extra S in % (Cal. from the Copper Contents).
1	78.73	21.09	1.40
2	78.77	—	1.35
3	78.74	—	1.39

stant within 2°. The composition corresponds to a true equilibrium, as the same composition is always reached no matter what the original percentage of sulphur may be.

The heating in hydrogen sulphide was always continued until the substance showed no change in composition after two successive heatings. Each heating lasted about six hours and for every heating the substances were reground. At high temperatures the equilibrium was reached more rapidly, but the lower temperatures required many successive heatings before it could be reached. The results are given in Table VI.

TABLE VI.

THE COMPOSITION OF COPPER SULPHIDE WHEN BROUGHT TO EQUILIBRIUM IN HYDROGEN SULPHIDE AT VARIOUS TEMPERATURES.

Temperature in C°.	Per Cent. Cu.	Per Cent. S by Difference.	Extra S in Per Cent.	Spec. Grav. 25°.
1050	78.52	21.48	1.66	5.675
700	78.47	21.53	1.73	5.666
485	78.09	21.91	2.20	5.638
410	77.53	22.47	2.90	5.562

As seen from this table the amount of sulphur in these substances increases with the decrease of temperature, while the specific gravity (given in the last column) decreases. In Fig. 73 the temperatures are plotted as abscissas and the percentage of extra sulphur as ordinates.

When copper sulphide is heated in hydrogen sulphide at still lower temperatures the sulphur content increases very rapidly, and at 358°, as will be shown later, is transformed into cupric sulphide.

This fact suggests that these substances may be mechanical

mixtures of cupric sulphide and its dissociation product, cuprous sulphide, a dissociation that may be expressed by the equation:

$$4\ CuS \rightleftarrows 2\ Cu_2S + S_2.$$

This reaction has recently been studied by Preuner and Brockmöller[14a] and will be discussed later. It may, however, be stated here that they found the dissociation curve to be very steep, and

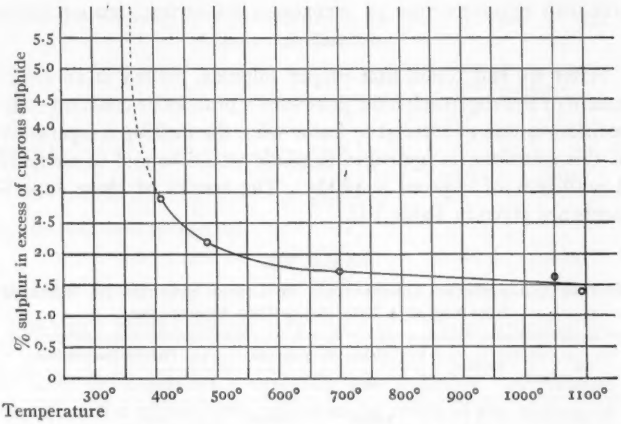

FIG. 73. Showing the composition of copper sulphide when brought to equilibrium in hydrogen sulphide at various temperatures.

extrapolating their results, the existence of unchanged cupric sulphide at temperatures around 1000° would not be expected. Furthermore, microscopic examination of melts made in hydrogen sulphide and in sulphur vapor by Graton and Murdock and by ourselves showed the products to be essentially[15] homogeneous. This fact also seemed to prove that these materials were not mechanical mixtures. Two other possibilities, furthermore, may be

[14a] *Z. phys. Chem.*, *81*, 129 (1912).

[15] Only one constituent was found, but in some preparations a slight mottling was observed which may be ascribed to slight variation in the composition of the mixed crystals formed during solidification.

suggested: (1) cuprous sulphide may dissolve sulphur. The case would then be analogous to that of pyrrhotite, which has been regarded, on the basis of work done in this laboratory, to be a solid solution of ferrous sulphide and sulphur.[15a] Or (2) these substances might be solid solutions of cuprous and cupric sulphides. Before, however, this question could be solved further experiments were necessary.

MELTING TEMPERATURE IN HYDROGEN SULPHIDE AND SULPHUR VAPOR.

After we had found that copper sulphide, melted in an atmosphere of hydrogen sulphide, possessed a practically constant composition, it was of interest to know what the melting temperature of this substance in hydrogen sulphide would be and to compare it with that of cuprous sulphide. The results of these experiments are given in Table VII.

TABLE VII.

MELTING AND FREEZING TEMPERATURES OF COPPER SULPHIDE IN HYDROGEN SULPHIDE AT A PRESSURE OF ONE ATMOSPHERE.

No.	Element.	Melting Temperatures.		Freezing Temperatures.	
		Mv.	°C.	Mv.	°C.
1	I	10631	1094	—	—
1	"	10642	1095	—	—
2	"	10668	1097	10507	1083
2	"	10659	1096	10566	1088
2	"	—	—	10466	1080
3	B	10655	1095	—	—
3	"	10669	1096	10507	1082

The *freezing* temperatures varied considerably as an undercooling seems to take place in these substances. The melting temperature, however, gives constant results, 1096°; about 34° lower than the melting point of cuprous sulphide.

To see whether the melting temperature and therefore the composition of these substances would be changed by raising the sulphur vapor pressure, we determined the melting point in sulphur vapor. To do so we put sulphur in the bottom of the ver-

[15a] Allen, Crenshaw and Johnson, *loc. cit.*

tical porcelain tube containing the crucible and surrounded the tube with two separately controlled furnaces, one resting on the other. The lower furnace was heated only high enough to boil the sulphur freely in the lower part of the tube. The crucible with the substance was suspended in the tube in the ordinary way within the central zone of the second furnace. The curves were taken in the usual way.

TABLE VIII.

MELTING TEMPERATURES OF COPPER SULPHIDE IN SULPHUR VAPOR AT ONE ATMOSPHERE PRESSURE.

	Temperature in Mv.	Mean Temperature.	
		Mv.	°C.
Element I	10220 10155 10211 10220	10201	1057
The same preparation the next day	10182 10148 10202 10222	10188	1056

The single results are not very constant. These irregularities are possibly due to variations in the sulphur vapor pressure, to which the melting point is evidently very sensitive. A pressure lower than the atmospheric might easily result if the boiling of the sulphur was not sufficiently vigorous. The average, however, represents probably very closely the true melting temperature, as two series of experiments taken on two different days gave the same average melting temperature. Freezing temperatures are not given, as no constant results could be obtained.

As seen from these experiments the melting temperature in sulphur vapor is about 39° lower than that obtained in hydrogen sulphide. The preparation (not rapidly cooled) was analyzed and found to contain 77.70 per cent. Cu, 22.30 per cent. S,[16] *i. e.*, about 1.3 per cent. more sulphur than the sulphide contained when it was chilled from above the melting point in hydrogen sulphide. If we assume that the composition of these substances did not change on cooling and the analyses correspond exactly

[16] Sulphur taken by difference.

to their composition at the freezing temperatures, we find that the lowering of the melting point is almost proportional to the

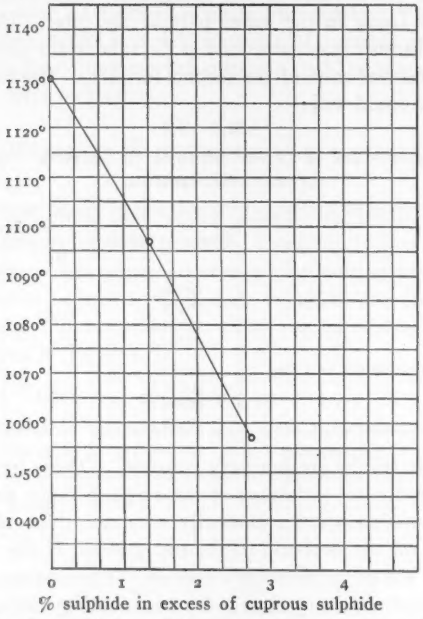

FIG. 74. The relation of the melting temperature of copper sulphide to the composition of the sulphide.

excess of sulphur present, calculated on the basis of cuprous sulphide (Fig. 74).

TABLE IX.

THE RELATION OF THE MELTING TEMPERATURE TO THE COMPOSITION OF THE SULPHIDE.

	Melting Temperature.	Lowering of the Melting Temp.	Per Cent. S in Excess (of Cu_2S).
Cuprous sulphide	1130°	—	0
Copper sulphide in H_2S	1096°	34°	1.40
Copper sulphide in S vapor at one atmosphere pressure	1057°	73°	2.70

The experiments show that the composition of these substances depends on the sulphur vapor pressure; but they do not allow us any direct conclusions, for when working with hydrogen sulphide, we also had a partial pressure of hydrogen present, the effect of which we do not know. We can state, however, from these experiments, that with decrease in temperature and increase of the sulphur vapor pressure the amount of sulphur in these copper sulphides increases and their composition lies within the limits of cuprous and cupric sulphides. The preparation in sulphur prepared by us contained 22.47 per cent. sulphur, but products higher in sulphur could probably be obtained under suitable conditions.

IDENTIFICATION AND DETERMINATION OF CUPROUS AND CUPRIC SULPHIDE WITH SILVER NITRATE.

In a recent paper[16a] from this laboratory a method has been described for the determination of cuprous and cupric sulphides in mixtures of the two. This method is based on the differences in the reaction products yielded by the two minerals when treated with silver nitrate. The two reactions are as follows:

$$Cu_2S + 4\ AgNO_3 = Ag_2S + 2\ Ag + 2\ Cu(NO_3)_2, \quad (1)$$
$$CuS + 2\ AgNO_3 = Ag_2S + Cu(NO_3)_2. \quad (2)$$

Cuprous sulphide gives equivalent amounts of silver sulphide and metallic silver, while cupric gives only silver sulphide. Separating the metallic silver from the silver sulphide by means of ferric nitrate and determining the amount of silver in both portions, the corresponding amounts of cuprous and cupric sulphide can be calculated.

Although the microscopic examination proved that the copper sulphides obtained by heating in hydrogen sulphide and sulphur vapor were not mechanical mixtures of cuprous and cupric sulphide, we thought their reaction with silver nitrate would possibly throw some light on their nature. We therefore treated the preparation obtained by heating in sulphur vapor, containing 77.70 per cent. Cu and 22.30 per cent. S, with silver nitrate, in the manner described.

[16a] Posnjak, *J. Chem. Soc.*, 36, 2475 (1914).

Product taken, 0.3392 g.

Metallic silver found .....0.3893 g. Ag.
Silver found in silver sulphide .....0.5022 g. Ag.

From these data, according to the method given, we calculate

$$\left.\begin{matrix} 0.2873 \text{ g. } Cu_2S \\ 0.0501 \text{ g. } CuS \end{matrix}\right\} \text{ or, } \left\{\begin{matrix} 85.17 \text{ per cent. } Cu_2S, \\ 14.83 \text{ per cent. } CuS. \end{matrix}\right.$$

If we assume that the substance taken consisted of cuprous and cupric sulphide and then calculate directly from its copper or sulphur content the percentage of the two sulphides, we get 83.95 per cent. Cu_2S and 16.05 per cent. CuS. This result differs from the one obtained by the silver nitrate method by 1.2 per cent., which is within the limits of accuracy of the method.

These facts would seem to favor the conclusion that the sulphides in question are composed of cuprous and cupric sulphide; and since the microscopic evidence indicates their homogeneity, they probably form a solid solution. However, if a solid solution of *cuprous sulphide* and *sulphur* were present, its reaction with silver nitrate might give similar results as would a mechanical mixture of the two sulphides. Such would be the case if the "dissolved" sulphur reacted completely with the metallic silver which forms in the reaction of cuprous sulphide with silver nitrate (see equation (1)). The reaction with silver nitrate is therefore not in itself sufficient proof that the sulphides in question are composed of cuprous and cupric sulphide, though that is the simplest interpretation of the reaction.

SPECIFIC GRAVITIES OF THE COPPER SULPHIDES.

As another means of identifying the nature of the products under discussion, we determined the specific gravities of several of our preparations and calculated from them the specific volumes (Table X.). On the basis of the analyses we also calculated what the percentage of cuprous and cupric sulphide would be, if the products were composed of these substances. Table X. contains also the specific gravities and specific volumes of pure cuprous and cupric sulphide.

TABLE X.

SPECIFIC GRAVITIES AND SPECIFIC VOLUMES OF THE COPPER SULPHIDES.

Per Cent. Cu.	Calculated.		Specific Gravities.		Spec. Vol.
	Per Cent. Cu_2S.	Per Cent. CuS.	25°	4° (Cal.).	
79.85	100.00	—	5.802	5.785	0.1728
78.97	93.28	6.57	5.743	5.726	0.1747
78.73	91.63	8.37	5.722	5.706	0.1753
78.60	90.66	9.34	5.689	5.672	0.1763
78.52	90.07	9.93	5.675	5.659	0.1767
78.47	89.69	10.31	5.666	5.649	0.1770
78.09	86.86	13.14	5.638	5.622	0.1779
77.70	83.95	16.05	5.612	5.596	0.1787
77.53	82.68	17.32	5.562	5.546	0.1803
66.46	—	100.00	4.697	4.684	0.2135

The results are plotted in Fig. 75. Within the limits of error the points fall on a line connecting the specific volumes of cuprous and cupric sulphides. This would be the case if the products consisted of mechanical mixtures. The same would be true if

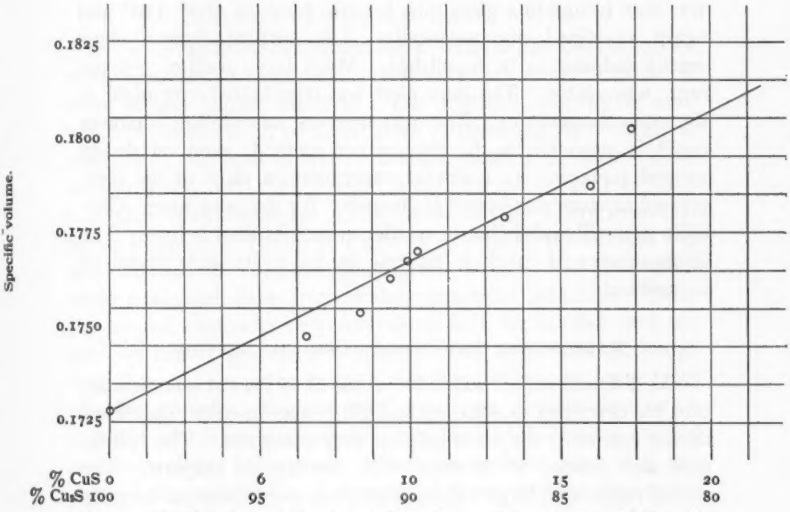

FIG. 75. Showing the variation in specific volume of the copper sulphide with calculated composition.

the products consisted of solid solutions which formed from the constituents without appreciable change in volume. While the case could not be decided from this evidence alone, the microscopic evidence indicates the correctness of the latter view.

SOLUBILITY OF CUPRIC SULPHIDE IN CUPROUS SULPHIDE.

We were able to prove more directly, in the following way, that cupric sulphide dissolves in cuprous sulphide. Very finely powdered pure natural chalcocite and covellite were mixed together in the proportions by weight of 9:1. This mixture was then compressed at about 1,200 atmospheres.[17] The compressed sulphide formed a hard coherent cake which could be easily polished and was examined microscopically. Covellite and chalcocite were both plainly visible. The amount of covellite, 10 per cent., thus estimated corresponded exactly to the composition of the original mixture. A fragment of this compressed mixture was then heated in a glass tube for two hours at 100°–110° and again examined microscopically. The surface showed some cracks and had to be repolished. Much less covellite, 3–5 per cent., was visible. The same piece was then heated over night at the same temperature. The next morning no covellite whatever could be detected by the microscopic method; even on deeply ground surfaces. In a similar experiment, a piece of the compressed mixture was heated at about 80° for the same time. Covellite was still visible, but in smaller quantities than before. The disappearance of covellite can only be due to its being dissolved in chalcocite.

MACROSCOPIC AND MICROSCOPIC DESCRIPTION.

The different copper sulphides prepared by the various methods thus far described showed marked differences in color; they were darker and bluer the more sulphur they contained. The brittleness also seemed to decrease with increase of sulphur. The cooled melts with large excess of sulphur were the most coarsely

[17] We wish to thank Drs. J. Johnston and L. H. Adams for their aid in the pressure work.

crystalline, and most ultimately traversed by octahedral parting planes. Polished surfaces revealed but one substance.[17a]

SUMMARY OF THESE RESULTS.

All these facts agree, and prove that cuprous and cupric sulphide form solid solutions. This would also explain the enormous lowering of the melting point of cuprous sulphide in hydrogen sulphide (34°), and in sulphur vapor (73°). For, assuming that the composition had not changed by the transition from the liquid to the solid state, we should have about 8.3 and 16.1 per cent. dissolved cupric sulphide, respectively, and this would be expected to exert no little influence on the melting point. As the experiment just described shows how readily such solid solutions may form, we believed it would be of interest from the geological standpoint to study more closely the composition of natural chalcocite.

ANALYSES OF NATURAL CHALCOCITES.

In the "Handbuch der Mineralogie" Hintze has collected about thirty analyses of chalcocite. However, they were all made on more or less impure material. The principal impurity is iron, which is present in all of them; some of these analyses contain as much as 17 per cent. of iron! Besides, most of the analyses are comparatively old. We thought it best for our purpose to make a number of new analyses of chalcocites of high purity from different localities. The specific gravity of some of the samples was also determined. The results are given in Table XI. The specimens examined were from widely separated localities. These samples of chalcocite represent about half the number sent us; the rest had to be rejected on account of impurities. Although even these are not perfectly pure, they contain but small quantities of other materials, in most cases some iron compounds (pyrite, bornite) which could be identified by the metallographic method and accordingly calculated. When the analyses were thus calculated, the ratio of Cu : S in seven of them, was found to corre-

[17a] Certain microscopic details are considered in the more complete description on p. 524.

TABLE XI.

ANALYSES AND SPECIFIC GRAVITIES OF CHALCOCITE.

Locality.	No.	Specific Gravity 25°.	Per Cent. Cu.	Per Cent. S.	Per Cent. Fe.	Per Cent. SiO_2.	Impurities Other than Fe and SiO_2.	Total.	Ratio Cu:S.[20]
New London, Frederick Co., Md.....	1	5.800	79.50	20.05	0.17[18]	0.17	—	99.89	2.012 : 1
Bristol mine, Conn.	2	5.797	79.65	20.02	—	0.06	Pb 0.20.	99.93	2.007 : 1
Butte, Mont. (a) exact locality unknown.	3	5.791	79.67	20.16	0.14[18a]	0.09	—	100.03	2.009 : 1
Butte, Mont. (b) Mountain View mine .	4	5.719	78.68	20.32	0.69[18a]	—	—	99.78	2.032 : 1
Descubredora Mine, Mexico	5	—	77.14	19.37	—	—	Fe_2O_3 1.92; rest silicate.	—	2.009 : 1
Cananea, Mexico.....	6	—	77.79	19.79	0.27[18a]	—	Rest silicate.	—	2.012 : 1
Morenci, Ariz.....	7	—	76.14	20.41	1.11[18a]	—	Mica 2.10.	99.76	2.006 : 1
Tularosa Dist., N. M.	8	5.710	78.96	20.62	—	—	Rest with part of the copper as malachite.	—	1.918 : 1
Bonanza mine, Alaska A.....	9	5.610	77.99	21.48	0.26[19]	0.13	—	99.86	1.848 : 1
Bonanza mine, Alaska B.....	10	5.606	77.56	21.55	0.55[19]	0.18	—	99.84	1.848 : 1

[18] In the form of bornite.

[18a] In the form of pyrite.

[19] Probably in the form of bornite.

[20] In calculating these ratios the impurities were first excluded.

spond practically to that in cuprous sulphide. The two samples of chalcocite from the Bonanza Mine, Alaska, and that from the Tularosa District, N. M., were found, however, to contain more sulphur than is demanded by ratio 2Cu : S.

OCCURRENCE OF SOLID SOLUTIONS OF CUPROUS-CUPRIC SULPHIDE IN NATURE.

The Alaska specimen B was sent to us by Professor Graton, who examined it microscopically and described it as follows:[20a] "This is a piece of the massive chalcocite from this great deposit. It is virtually pure and is the purest chalcocite which we have found in any quantity. It consists of fields of homogeneous color surrounded by an aggregrate of small grains of mottled color ranging from pinkish to bluish. These portions of varying color constitute only 2 per cent. or 3 per cent. of the whole and do not seriously reduce the purity of the material. Furthermore, all of the material is chalcocite as we define it and such ranges in color we find rather frequently." In a later communication Graton and Murdock, after a careful study with the oil immersion objective, stated that particles of bornite and exceedingly minute particles of chalcopyrite, the latter a very small fraction of one per cent., could be seen, and in addition to this, the chalcocite itself was mottled. Let us assume that all the iron is present as bornite, and calculate it in this way. Bornite has the formula Cu_5FeS_4. Therefore, 0.55 per cent. Fe (see Table XI.) is equivalent to 3.13 per cent. Cu and 1.26 per cent. S. This would make altogether 4.94 per cent. bornite. We have left then 74.43 per cent. Cu and 20.29 per cent. S. Now, if all this copper were present as cuprous sulphide it would require 18.78 per cent. sulphur leaving 1.51 per cent. still unaccounted for.

In the Alaskan sample, A, a small amount of free covellite could be detected microscopically. We estimated it at about 1–2 per cent. If the iron (0.26 per cent.) were calculated as bornite (2.34 per cent.) and the 2 per cent. of visible covellite taken into account, there would remain 75.18 per cent. Cu and 20.21 per cent. S. To form chalcocite the copper, however, would require

[20a] Private communication.

only 18.95 per cent. S, leaving 1.26 per cent. S unaccounted for.

Judging from our previous work such an excess of sulphur must be present as cupric sulphide and since the microscopic examination disclosed no covellite in sample B, and an insufficient quantity in A we conclude that this cupric sulphide is all dissolved in the former and partly in the latter.

If the minerals are calculated in this way we shall find 7.8 per cent. of the copper sulphide in A and 9.4 per cent. in B is dissolved cupric sulphide. If the analyses are expressed in proximate form we have

	A.	B.
Quartz	0.13	0.18
Bornite	2.34	4.94
Covellite	2.00	—
Dissolved CuS	7.45	8.92
Dissolved Cu_2S	88.08	85.96
	100.00	100.00

If the volume of the two minerals is equal to the sum of the volumes of the constituents of each, giving to bornite the specific gravity 5.076,[21] to quartz the specific gravity 2.65 and to chalcocite and covellite[21a] the values in this paper, we obtain the values in Table XII.

TABLE XII.

SPECIFIC GRAVITIES OF ALASKAN CHALCOCITES WHICH CONTAIN EXCESS OF SULPHUR OVER THE RATIO 2Cu : S.

	Specific Gravity. Calculated.	Determined.
Bonanza Mine, Alaska A	5.646	5.610
Bonanza Mine, Alaska B	5.630	5.606

The agreement is only approximate, but the presence of iron only in the form of bornite is an assumption. At any rate the gravities are markedly lower than ordinary chalcocite and are like those of synthetic solid solutions. Moreover, the color of the specimens and their thermal behavior, as we shall see later are in accord with the hypothesis that we have here cupric sulphide-chalcocite solid solutions.

[21] Allen and Crenshaw, unpublished data.

[21a] It will be remembered that covellite has practically the same volume as dissolved cupric sulphide.

A microscopic examination of the chalcocite from the Tularosa District, N. M., showed that malachite was the only visible impurity.[22] The exactness of the determinations of the total copper and sulphur enables us to calculate this malachite very satisfactorily thus:

$$100\% - (\% \text{ S} + \% \text{ Cu}) = \% \text{ } (OH)_2CO_3 = a$$

$$a \cdot \frac{Cu_2(OH)_2CO_3}{(OH)_2CO_3} = \% \text{ malachite.}$$

0.99 per cent. malachite was found. Subtracting the malachite we have left 78.39 per cent. copper and 20.62 per cent. sulphur. The ratio 2Cu : S demands for 78.39 per cent. copper, 19.78 per cent. sulphur, leaving 0.84 per cent. sulphur. The homogeneity of the sulphide proves that we have again a cupric sulphide-chalcocite solid solution. Calculated as such we obtain 93.98 per cent. cuprous sulphide and 5.03 per cent. cupric sulphide. Allowing for 0.99 per cent. malachite with specific gravity of 4.1, we calculate 5.709 for the aggregate, while experiment gave 5.710.

In this connection the two copper sulphides digenite and carmenite may be mentioned. Digenite has been found in several localities and is described by Breithaupt[22a] as a compound of the composition $2Cu_2S.CuS$. Carmenite was described by Hahn[23] as having the composition $Cu_2S.CuS$. A mineral of smiilar composition was also described by Lindström.[24] Dana[25] examined a sample of carmenite and detected in it a visible amount of covellite. He, therefore, believed that these substances were mixtures of chalcocite and covellite. But it is quite possible that some of these specimens may also contain cupric sulphide in a dissolved condition.

Covellite and chalcocite are often closely associated in nature; mere contact at low temperature is apparently not sufficient for the formation of solid solutions of them. However, the great

[22] It was, however, "mottled" like the synthetic chalcocite that contained an excess of sulphur.

[22a] *Pogg. Ann., 61,* 673 (1844).

[23] *B. H. Ztg., 24,* 86 (1865).

[24] *Geol. För. Förh., 7,* 678 (1885).

[25] "System of Mineralogy."

readiness with which solution has been shown to take place raises the question whether such solutions are not common in nature. Chalcocites are generally too impure, as we have seen, to decide the question by chemical means, but the variation in the color of natural chalcocites under the microscope is to our minds suspicious and it is suggested that a careful microscopic comparison of the colors of natural chalcocites with the synthetic solutions of known concentration, especially comparisons made with a comparison eye-piece might be fruitful. The thermal method described on pages 513–520 has also been found suitable for distinguishing between ordinary chalcocite of the formula Cu_2S and solid cupric sulphide solutions even in intermixtures of other minerals. The limitations of the method are considered in the proper place.

THE NATURE OF PYRRHOTITE IN THE LIGHT OF THESE EXPERIMENTS.

In a previous paper from this laboratory ("The Mineral Sulphides of Iron," Allen, Crenshaw & Johnston) dealing with the mineral pyrrhotite, the conclusion was reached that pyrrhotite is a solid solution of sulphur in ferrous sulphide. The facts which supported this view are as follows: The pyrrhotites of nature are of variable composition, and the synthetic pyrrhotites form a continuous series; sulphur is absorbed or lost according to the temperature and pressure of the sulphur vapor in which they are heated. The range in composition and specific gravity of these solutions agreed well with those known in nature. When either natural or synthetic pyrrhotites are treated with dilute acids (hydrochloric or sulphuric) the products are ferrous salt, hydrogen sulphide and sulphur. Now, the experiments on the copper sulphides show the existence of substances both natural and synthetic which in many respects are analogous to the pyrrhotites, and here it is difficult to escape the conclusion that the solutions contain cupric sulphide. Do the pyrrhotites similarly contain a higher sulphide of iron dissolved in ferrous sulphide? If they contained disulphide of iron, this and not sulphur should remain when pyrrhotite is dissolved in a non-oxidizing acid. No other sulphide of iron is known with certainty, but the facts concerning the

cupric sulphide-chalcocite solutions would give an added interest to a search for ferric sulphide.

ISOMETRIC AND ORTHORHOMBIC CUPROUS SULPHIDE.

INVERSION OF CUPROUS SULPHIDE BY THE THERMAL METHOD.

As has been previously stated, faceted crystals of cuprous sulphide occur in nature, as far as known only in the orthorhombic form; while at high temperature, synthetic cuprous sulphide is always obtained in isometric crystals. It is therefore dimorphous. Hittorff,[26] in a study of the temperature effect on the electrical conductivity of cuprous sulphide, observed a sudden change at about 103°. He also studied the heat effect by taking cooling curves and found a discontinuity with one preparation at 97°, with another at 79°. More recently Mönch[27] has studied the electrical conductivity of compressed powders of both synthetic (isometric), and natural cuprous sulphide from Bristol, Conn. Both behaved in essentially the same way, but he found two breaks in his curves: in one at 95° and 150° and in the other at 103° and 167°. Reichenheim[28] called attention to the irregularities of the temperature resistance curves of compressed powders, and among other substances also studied the electrical conductivity of solid rods of synthetic cuprous sulphide. He confirmed the first inversion point as between 89° and 98°, but could not find a second inversion mentioned by Mönch. In the region of the first point Bellati and Lussana[29] found also a change in the specific heat.

We studied this change by the thermal method using a copper-constantan thermoelement.[30] Besides the ordinary temperature-time curves we applied also Roberts-Austen's differential device,[31] using as a neutral body copper oxide. The substance (5–10 gr.) was placed in a small glass tube and heated by means of an oil-bath. Of the five preparations used, three were very pure natural

[26] *Loc. cit.*

[27] *N. Jahrb. f. Min.*, 20, 365 (1905). Beilg.-Bd.

[28] Inaugural Dissertation, Freiburg, 1906.

[29] *Atti. Instit. Venet.*, 7, 1051 (1890).

[30] Adams and Johnston, *Am. Journal of Science*, (4) XXXII., 534, 1912.

[31] See C. K. Burgess, Bull. Bureau Standards, V., p. 210, 1908–9; W. P. White, *Amer. Jour. Sc.*, XVIII., 453, 1909; *Zeit. anorg. Chem.*, 69, 349, 1911.

chalcocites (see analyses nos. 1, 2, 3, Table XI.), and two pure synthetic cuprous sulphides. Like Mönch, we also found that natural chalcocite and the synthetic products behaved in the same manner, but found in our curves only one break.

The earlier heating curves, however, seemed to contain two breaks: one at 91° and another somewhat higher. The latter varied with the rate of heating and was sometimes 12° higher than the first one. Experiments showed plainly that this second point was due merely to a retardation of the inversion in the coarser grains of the material, for, when the material was finely ground in a mechanically driven mortar, this point completely disappeared. This is shown in Fig. 76. The material used was

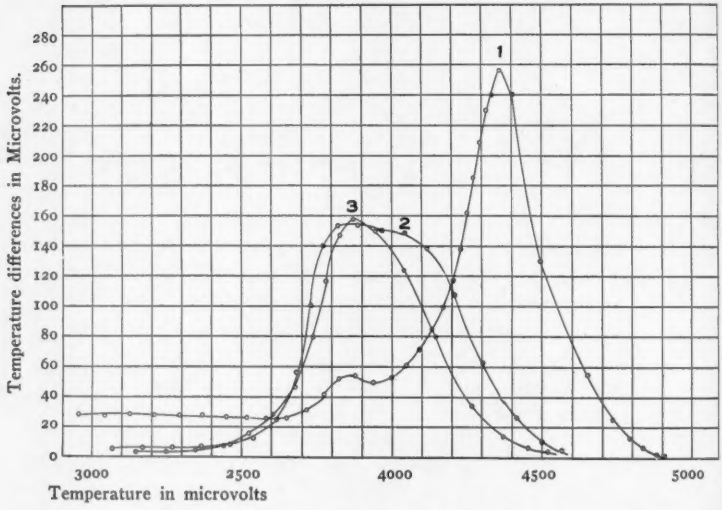

FIG. 76. The inversion temperature of chalcocite and its dependence upon the size of the grains.

chalcocite from Butte, Mont. (Table XI., no. 3). The material used for curve I was sized between 100- and 125-mesh per linear inch. The curve shows two maxima; a slight one at about 91°

and a very pronounced one at about 102°. The first represents the real inversion point and was doubtless due to very fine powder of the material that clung to the coarser grains; but as there was comparatively little of this, it produced only a small heat effect. The greater part of the material was in coarse grains and the inversion was retarded, but when it took place a much larger heat effect was produced.

The material used for curve II. passed through a 200-mesh (per linear inch) sieve, though it doubtless contained all grades of fineness below that size. The curve reaches a maximum at about 91° but continues flat for a while, showing, as might be expected, that the inversion takes place through an interval. Finally, the material used for curve III. was ground for two hours in a mechanically driven mortar and was extremely fine. The curve again reaches a maximum at about 91° and then rapidly falls off.

This retardation effect due to coarseness of the material is in accordance with the theory that the amount of free energy involved in passing from one form to the other is dependent upon the size of grains.

All the substances subsequently studied by this method were finely ground in a mechanically driven mortar and gave perfectly sharp heat effects. In each single preparation the inversion point did not vary more than one degree, but was always lower on the cooling than on the heating curve. In Table 13 both these temperatures are given. Each is the average of several experiments. Some typical temperature-time curves are given in Table XIV.

TABLE XIII.

INVERSION TEMPERATURE OF PURE NATURAL AND SYNTHETIC CUPROUS SULPHIDE

Substance.	Heating.	Cooling.
Frederick Co., Md.	91.5°	—
Bristol, Conn.	90.0°	86.5°
Butte, Mont.	91.3°	84.6°
Synthetic Cu_2S, I	90.7°	88.0°
Synthetic Cu_2S, II	91.4°	87.0°

Heating experiments were also extended to higher temperatures. No other heat effect whatever could be detected up to 210° and

the thermal method did not confirm Mönch's statement that cuprous sulphide undergoes a second inversion at about 160°.

INVERSION OF CUPROUS SULPHIDE BY THE ELECTRIC CONDUCTIVITY METHOD.

In view of the fact that inversions may sometimes be detected by one method while they can not be detected by another (*e. g.*, the inversion of chalcocite at 91° can not be detected by the dilatometric method[32]), the second inversion of chalcocite found by Mönch, however doubtful according to Reichenheim's work, still remained a possibility.[33] The existence of a third form of cuprous sulphide would be of much importance in the study of the genetic conditions of chalcocite. It was therefore necessary to ascertain the facts by a repetition of the conductivity measurements of chalcocite.

The measurements were made with the Wheatstone Bridge and alternating current from the secondary of an induction coil. Pieces of chalcocite were cut into rods, and their ends polished. To these polished surfaces two gold electrodes were pressed tight by means of a stiff spring and a clamp. The whole was then placed in a well stirred oil-bath, heated by means of an electric resistance coil wound around the bath. The temperature of the bath (measured with copper-constantan thermo-elements) was perfectly uniform and could be kept constant for any length of time.

In accordance with previous observers we found that the conductivity of different chalcocites varied very much. However, the resistance of our solid pieces did not change after being heated, like the compressed powders which Mönch used, but remained constant for definite temperatures. As we were looking merely for the change in the resistance with temperature, the absolute resistance did not matter much, and no effort, therefore, was made to get chalcocite of the highest resistance. The three pieces

[32] Sahmen and Tammann, *Ann. d. Phys.*, *10*, 879 (1903).

[33] Groth in his book "Chemische Krystallographie" I, p. 135, doubts that the inversion from othorhombic into isometric chalcocite takes place at the 91° inversion point.

we selected were as follows: (1) Chalcocite from Cananea, Mexico, which had a specific resistance of about 17,000 ohms (25°); (2) synthetic cuprous sulphide of the specific resistance of about 3,200 ohms (25°) and (3) chalcocite from the Bonanza Mine, Alaska, which had a specific resistance of about 900 ohms (25°).

The results obtained are given in Fig. 77. The first branch of

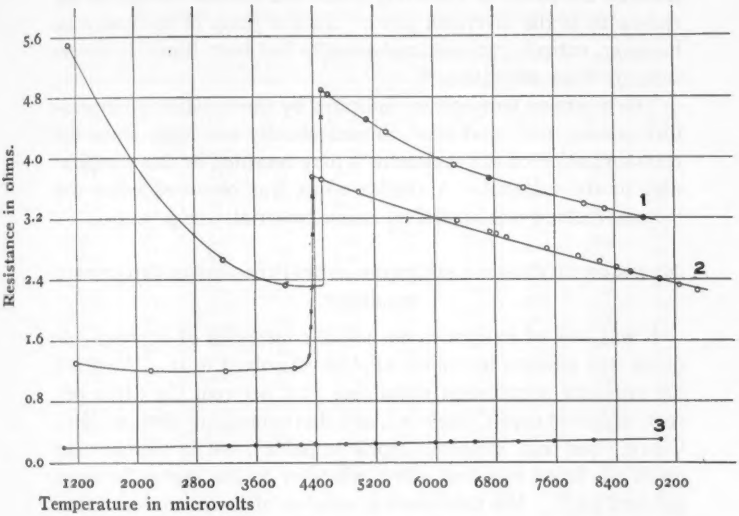

FIG. 77. Showing the change in resistance with temperature of (1) chalcocite from Cananea, Mexico; (2) synthetic chalocite and (3) chalcocite from the Bonanza Mine, Alaska.

curve 1 is much steeper than the corresponding one in curve 2 (natural chalcocite from Cananea, Mexico, and synthetic cuprous sulphide, respectively), which is possibly due to unipolarity. At about 104° and 102°, respectively, both show a sudden increase in resistance, after which the resistance falls off with increasing temperature (followed up to 200°), and the two curves run almost parallel. *No break occurs in the curves after the inversion at about 104°* and Mönch's statement of a discontinuity in the curve

about 160° must be regarded as due to some experimental error. Furthermore, Mönch found that above the inversion at 104° the temperature coefficient of the resistance was positive, while our experiments in agreement with Bodländer and Tdaszewski[34] and Reichenheim[35] show that the temperature coefficient of the resistance above the inversion is negative. It is surprising that none of the previous observers found the sudden change in the resistance at the inversion point. Such a jump in resistance is, however, entirely rational, and actually had been found in inversions of other substances.[36]

The inversion temperature indicated by the resistance-temperature curves, 104° and 102°, is undoubtedly too high, since the transformation of the chalcocite is here retarded by the compactness of the material. A similar effect was observed when the thermal method was applied to coarse material (see p. 514).

INVERSION OF CUPROUS SULPHIDE CONTAINING DISSOLVED CUPRIC SULPHIDE.

It was now of interest to see how the inversion of cuprous sulphide was affected by cupric sulphide dissolved in it. We tried the synthetic preparation containing 77.7 per cent Cu (16.0 per cent. dissolved cupric sulphide), and that containing 78.6 per cent. Cu (9.3 per cent. dissolved cupric sulphide), but in neither case could we detect any heat effect whatever in the region between 30° and 135°. We then made a solution of lower concentration by heating finely powdered cuprous and cupric sulphide in known proportions. These mixtures were first compressed under about 10,000 atmospheres forming a hard coherent cake. Polished surfaces of such compressed mixtures showed covellite plainly, but after they were heated several hours at about 110° all the covellite disappeared and their homogeneity showed that solution had taken place. For the determination of the inversion temperature these preparations were finely ground. Typical curves for some of the preparations are given in Table XIV. Curves for pure

[34] *Loc. cit.*
[35] *Loc. cit.*
[36] Koenigsberger and Schilling (4), 32, 179 (1910).

natural and synthetic chalcocite are also included in this table. The numbers represent the electromotive force of the thermoelement at intervals of one minute, together with a column of differences at the right of each record.

TABLE XIV.

THE INVERSION OF CUPROUS SULPHIDE, NATURAL AND SYNTHETIC, WITH AND WITHOUT CUPRIC SULPHIDE. TEMPERATURE-TIME CURVES.

Pure Synthetic Cuprous Sulphide.		Chalcocite from Butte, Mont.		Cuprous Sulphide Containing 3 Per Cent. Dissolved Cupric Sulphide.		Chalcocite from the Tularosa Dist., N. M.		Chalcocite, Bonanza Mine, Alaska.	
M.V.	D.V.	M.V.	D.V.	M.V.	D.V.	M.V.	D.V.	M.V.	D.V.
3,557	60	3,445	93	3,456	71	3,381	72	3,425	49
617	54	538	86	527	69	453	71	474	48
671	49	624	83	596	67	524	68	522	48
720	48	707	72	663	65	592	65	570	46
768	42	779	59	728	60	657	63	616	45
810	37	*838*	45	788	58	720	61	661	43
847	34	883	47	846	53	781	56	704	43
881	52	930	54	899	49	837	51	747	41
993	75	084	72	*948*	48	888	42	788	41
4,008	92	4,056	89	996	52	930	34	829	39
100	85	145	105	4,048	68	*964*	31	868	38
185	70	250	120	116	85	995	49	906	37
255	59	370	99	201	73	4,044	96	943	35
314	57	469	83	274	62	140	75	978	35
371	53	552	68	336	57	215	60	4,013	34
424	50	620	64	393	54	275	54	047	32
474	49	684	60	447	51	329	49	079	32
523		744		498	50	378	48	111	31
				548	47	426		142	29
				595				171	29
								200	27
								227	

The actual inversion temperature of different cupric sulphide-chalcocite solutions is given in Table XV.

TABLE XV.

INVERSION TEMPERATURE OF CUPRIC SULPHIDE-CHALCOCITE SOLUTIONS.

Composition.	Temperature.
Inversion of Cu_2S	91.1
97 per cent. $Cu_2S + 3$ per cent. CuS	93.1
95 per cent. $Cu_2S + 5$ per cent. CuS	93.4
94 per cent. $Cu_2S + 6$ per cent. CuS	93.6
Nat. chalcocite from the Tularosa Dist., N. M. (contains 5 per cent. CuS).	93.3

Preparations containing eight or more per cent. of dissolved cupric sulphide showed no heat effect at all. Likewise no heat effect could be observed with the chalcocite from Alaska, which, as we stated above, must contain about 9 per cent. dissolved cupric sulphide. This was also confirmed by the electrical conductivity method as seen from curve 3, Fig. 77. While the chalcocite from the Tularosa District, N. M., as given in Table XIV. showed the heat effect at 93.3°—the same temperature as that given by a synthetic solution containing 5 per cent. cupric sulphide. These facts seem to further support our assumption, that the two named chalcocites are solid solutions of cuprous and cupric sulphide.

The disappearance of the heat effect in preparations containing more than about eight per cent. dissolved cupric sulphide is very strange. It is not due to a simple "dilution" of the heat-effect. For, when we admixed even 15 per cent. finely powdered bornite to the cuprous sulphide the heat effect was still easily detected. An analogous case of the disappearance of the heat effect is already known in pyrrhotite, but the explanation given for it by Rinne and Boeke,[37] that the inversion takes place, but is too sluggish to be observed, is probably not sufficient. From the fact that two methods in our case gave no indication whatever that an inversion takes place, it seems more probable that the substance did not invert. This view is also supported by the crystallographic evidence, which will be given later. A further investigation of such phenomena is desirable.

FORMATION AND DESCRIPTION OF CUPROUS SULPHIDE CRYSTALS.

CUPROUS SULPHIDE FORMED IN THE DRY WAY.

To prove that the inversion point found by us at about 91° is really due to the change of orthorhombic into regular cuprous sulphide, we attempted to form crystals above and below that temperature.

We obtained isometric cuprous sulphide in well-developed crystals by heating copper sulphide in vacuo a little below its melting point. Cuprous sulphide crystals were also formed by heating copper in sulphur vapor. For this purpose sulphur was first in-

[37] *Zs. anorg. Chem., 53,* 338 (1907).

troduced into a Jena glass tube; a smaller inner tube containing the copper was then put in, and the tube was finally evacuated and sealed. For convenience it was heated in a steel bomb.

The crystals form at temperatures as low as 125°, but it is only above about 275° that the crystals have been large enough and sufficiently separated to allow determinations of symmetry. Above about 350° crystals of only one distinct habit have been observed, the cubo-octahedron. This form may be flattened parallel to an octahedral face, producing thick hexagonal plates. The octahedral faces are nearly always striated parallel to the sides. Twinning with the composition plane parallel to the octahedron is common. Between 275° and 350° skeletal crystals commonly appear with the cubo-octahedron. Measurements on the goniometer established the isometric symmetry of some crystals grown from a copper wire in sulphur vapor at 280°.

CUPROUS SULPHIDE FORMED FROM SOLUTIONS.

In the wet way cuprous sulphide was prepared by heating cuprous chloride with a 10 per cent. solution of sodium sulphide in a sealed evacuated glass tube. An amorphous precipitate is formed as soon as the two are brought together; but on heating the tube for about eight days at 250° well developed crystals of cuprous sulphide are obtained. The analyses gave 79.45 per cent. Cu and 20.61 per cent. S, indicating a small amount of cupric sulphide present, due probably to oxidation of the cuprous chloride or the freshly precipitated cuprous sulphide. The crystals were well defined octahedra, slight modified by the cube. The octahedral faces were in many cases decidedly stepped off, in others scarcely more than striated. We tried the same method at 125°, but no crystals were formed during a month.

Minute crystals resembling cuprous sulphide were also formed by heating copper with sodium thiosulphate at about 110°; they were too small, however, to be identified.

As cuprous sulphide appeared to be somewhat soluble in hydrogen sulphide water, attempts to form crystals by recrystallization from it were also made. We used natural (Butte, Mont.) as well as synthetic cuprous sulphide. Tubes containing water saturated

at 0° with hydrogen sulphide and powdered cuprous sulphide were sealed up and heated for several days at various temperatures. Well developed crystals were formed in tubes heated at 200° and 170°, respectively. They were measured and proved to be isometric. Very small crystals, apparently cubo-octahedra, were also found in a tube heated nine days at 125°.

CRYSTALS FORMED BY THE ACTION OF AMMONIUM SULPHIDE ON METALLIC COPPER AND ON CUPROUS SALTS.

Several authors assert that cuprous sulphide crystals are formed by the action of ammonium sulphides on copper, under exclusion of air. Thus Merz and Weith[38] report the formation of orthorhombic cuprous sulphide by the action of yellow ammonium sulphide on copper plated with platinum. Heumann[39] reports the formation of gray crystalline needles, that have metallic lustre and the composition of cuprous sulphide, by the action of colorless ammonium sulphide on copper. He found this reaction to be accompanied by an evolution of hydrogen and a considerable quantity of copper dissolved in the liquid. Priwoznik[40] also confirms these observations.

We repeated these experiments and obtained crystals (described below) closely resembling cuprous sulphide in color, by treating copper[41] with ammonium sulphide at various temperatures (up to 125°) in evacuated tubes. These crystals form very readily even at room temperature, under evolution of a gas and much copper is found in solution indicating a considerable solubility of these crystals in ammonium sulphide. Larger quantities of well-developed, but smaller crystals of the same composition are obtained when cuprous chloride dissolved in concentrated ammonia and carefully protected from oxidation is subjected to the action of hydrogen sulphide. A voluminous amorphous precipitate is immediately formed, but if hydrogen sulphide is continuously passed through the solution, the precipitate becomes crystalline at room temperature within about twenty minutes.

[38] *Zeitschr. f. Chem., 12,* 241 (1869).
[39] *Ann. d. Chem., 173,* 22 (1874); *Ber., 6,* 21 (1873).
[40] *Ber.,* 1291 (1873); *Ann., 171,* 111 (1874).
[41] Part of the copper was always found unchanged.

The same crystalline product is also obtained when cuprous sulphide is left to stand in a closed tube with ammonium sulphide.

All these preparations, however, proved to be not cuprous sulphide, as has been asserted by previous observers, but a compound containing besides copper and sulphur also ammonium. This is shown in the following analyses of several preparations:

TABLE XVI.

COMPOSITION OF CRYSTALS FORMED FROM AMMONIUM SULPHIDE SOLUTIONS.

No.	1	2	3	Calculated for $Cu_7(NH_4)S_4$
Cu	75.19	75.18	75.39	75.25
S	21.65	21.46	—	21.67
NH_4	3.04	—	—	3.06
Total	99.88	—	—	100.00

According to these analyses the composition of the crystalline compound is $Cu_7(NH_4)S_4$.

Crystals from several preparations were measured. In one of them formed at ordinary temperature from metallic copper, the crystals were rough prisms with a maximum size of 2×0.5 mm. Out of fifty only three were suitable for measurement. In another preparation the crystals were much smaller but very lustrous. The largest were needles about 3 mm. long and 0.1 mm. in diameter. Twelve were measured. No differences were found between the angles of the two preparations. All were tetragonal prisms terminated by a rough base and a trapezohedron. Although both terminations of no single crystal were measured, microscopic examination showed the double termination and no plane of symmetry. Two prisms, (100) with narrower faces minutely striated longitudinally, and (110) were found. The trapezohedron was found over the ditetragonal prism (410) which was not observed. From 12 good signals the average observed angle $(001) \wedge (411)$ was 57° 33′. The extreme values were 57° 9′ and 57° 47′. For the angle $(100) \wedge (410)$ the corresponding values were 13° 55′, 14° 40′, 13° 30′. This angle is theoretically 14° 2′. Thus $c = 1.526$. Both right-handed and left-handed crystals were found.

In another lot of microscopic crystals formed at 80°, square prisms were found each terminated by a steep pyramid making an angle of $24° \pm 1°$ with the vertical axis. These crystals correspond to the unit prism (110) and the unit pyramid (111) of the measured crystals.

CRYSTALLOGRAPHIC RELATIONS OF THE ISOMETRIC AND ORTHORHOMBIC FORMS OF CUPROUS SULPHIDE.

PARTING AND ETCH-CLEAVAGE.

Measured and oriented chalcocite *crystals* from Bristol, Conn., showed no trace of the reported prismatic cleavage, not even when etched. An apparent basal cleavage was observed on three crystals, but it was not detected on several others. Subparallel or possibly twinned groups have a basal pseudocleavage.

Known faces of several of these crystals were etched in nitric acid of various concentrations. A very pronounced basal etch-cleavage developed on every face which was not too nearly parallel to the base. On the base a distinct but much poorer etch-cleavage was observed parallel to the front pinacoid. On sections sufficiently inclined to the base to permit good development of the basal etch-cleavage the front pinacoidal etch-cleavage may practically disappear. Very few grains of the purer massive chalcocite and of synthetic aggregates resulting from melts in vacuo show more than the one set of etch lines.

No distinct etch-cleavage appears in the *isometric high temperature form of cuprous sulphide.* Many attempts were made to produce such a cleavage by etching natural and artificial preparations at 100° or over after they had been held at 120° for several minutes. Both dilute nitric acid, and concentrated sulphuric acid to which about one tenth of its volume of nitric acid of various concentrations had been added, were used. The only etching produced appeared to follow structures already present in the crystals before they had been heated, such as pseudo-cleavage and incipient cleavage in the natural crystals, and as octahedral parting planes also in synthetic crystalline grains.

Etch-cleavage and the etching out of parting planes are very different. Lines of parting are in reality straight boundaries

between grains, and they etch out like such boundaries. Only a limited number, which are usually much wider and much less interrupted than cleavage lines, can be present.

Cuprous sulphide containing more than about 8 per cent. of dissolved covellite, if formed at high temperature, when etched at ordinary temperature does not have the characteristic etch-cleavage of the orthorhombic form (chalcocite) but planes of octahedral parting etch out more or less clearly. Such parting is more pronounced in masses cooled after fusion, especially if a large amount of dissolved covellite is present. This evidence that no inversion takes place in these solid solutions, combined with similar evidence from heating curves and conductivity measurements, is very convincing. If less than about 8 per cent. of covellite is present the orthorhombic etch-cleavage due to inversion does develop at ordinary temperatures, as one would expect from the thermal data. If solid solutions containing even 15 per cent. of covellite could be crystallized at temperatures just below 91° they would probably etch like ordinary chalcocite.

RELATIVE ORIENTATION.

If an isometric crystal formed at high temperature is etched at ordinary temperature after it has inverted to the orthorhombic form, the orthorhombic basal etch-cleavage is found to have a definite relation to the isometric axes, even though the original crystal may be after inversion an aggregate of several orthorhombic individuals. On an octahedral face these cleavage lines of each new grain are normal to one of the edges of the octahedron; on a cube face they are parallel to an edge or a diagonal. Thus the base of the orthorhombic crystal corresponds to a dodecahedral plane, and six differently oriented crystals may all have the same orientation with respect to the isometric axis. If we assume further that the *a*-axis of the orthorhombic crystal is one of the isometric axes, then all the principal forms of the two crystals come nearly or quite to coincidence. The maximum divergence, 5°, is between the prism (120) and the corresponding dodecahedral faces. This divergence may be compared with the 10° divergence between the bases of the two monoclinic pyroxenes diopside and wollastonite.

APPLICATION OF DATA TO GEOLOGY.

The work of the foregoing pages has established two points of special interest to geology. First, it has proved the existence of natural chalcocites which contain a larger percentage of sulphur than cuprous sulphide, due to the presence of cupric sulphide in a condition of solid solution. These chalcocites are darker in color and lighter in gravity than the ordinary variety. In the identification of the new variety, color is helpful though perhaps not always certain. Analysis and gravity often fail because of impurities which are very generally present in chalcocite. Chalcocites containing more than 8 per cent. of dissolved cupric sulphide are readily detected by the thermal method which then shows no absorption of heat at 91°. When less than 8 per cent. cupric sulphide is present the inversion point (91°) is raised but so slightly that the results may be indecisive.

Although these dark cuprous sulphides have been prepared synthetically in several different ways our knowledge of their genetic conditions is still insufficient to explain their formation in nature, but a further study of them both in the laboratory and in the field may be expected to yield interesting returns.

Secondly it has been shown in this paper that orthorhombic cuprous sulphide, chalcocite, of the ordinary composition (Cu_2S) passes into an isometric form at 91° and is therefore stable only below that temperature. Within this range of temperature deposits of secondary chalcocite have in all probability formed.[42]

Although it might be inferred from certain mineralogical associations that primary cuprous sulphide should have been formed at temperatures above about 91°, yet all observed faceted crystals of this substance have been orthorhombic. Search should be made for isometric crystals. There is some evidence that certain massive ores do contain isometric cuprous sulphide, and may thus be in part primary. The photograph by Graton and Murdoch[43] of the ore from the Bonanza Mine, Alaska, shows etched structures like the octahedral parting sometimes seen in artificial cuprous

[42] See W. H. Emmons, ECON. GEOL., *10*, 151 (1915).
[43] *Trans. Am. Inst. Min. Eng.*, *45*, 78–79 (1914).

sulphide of the isometric (high temperature) form. It is further significant that analyzed samples of the Bonanza ore show about nine per cent. of dissolved cupric sulphide, a quantity sufficient to prevent isometric crystals which may have formed above 91° from going over into the orthorhombic form as cooling progressed. Etched surfaces of some of the analyzed samples of this ore contain grains in irregular veins which etch like chalcocite (orthorhombic) and are thus shown to be the low temperature form. They may have formed above 91° and contain too little cupric sulphide to prevent their inversion, or they may have formed below the temperature of inversion.

In a compact ore which contains less than about 8 per cent. of dissolved cupric sulphide it might not be possible to tell whether the temperature of formation was above or below the inversion temperature, for such ores are always granular chalcocite when observed, and structures which were present in the isometric form may have been destroyed.

CUPRIC SULPHIDE (COVELLITE).

FORMATION OF CUPRIC SULPHIDE.

Cupric sulphide can be formed in many different ways. As was mentioned above, cupric sulphide forms from cuprous sulphide in an atmosphere of hydrogen sulphide at temperatures up to 358°. In the same way it can be formed from metallic copper.

As the stability of cupric sulphide at higher temperature depends on the surrounding sulphur vapor pressure, it can be easily prepared at those temperatures if only the surrounding sulphur vapor pressure is kept equal to or greater than the dissociation pressure of cupric sulphide at the chosen temperature. Thus we prepared cupric sulphide by heating copper or cuprous sulphide in a sealed evacuated tube over sulphur. In all these cases the cupric sulphide is crystalline and of deep blue color.

Cupric sulphide is formed in the wet way when a cupric salt is precipitated with hydrogen sulphide. A 2.5 per cent. solution of copper sulphate containing 1 per cent. sulphuric acid was precipitated with hydrogen sulphide, the precipitate washed with hydro-

gen sulphide water and dried in vacuo. Two products made in this way gave 99.7 per cent. and 99.4 per cent. cupric sulphide respectively. Since the copper was lower than the theoretical amount required by cupric sulphide, no cuprous sulphide could have been present. Statements[44] found in the literature, that cupric salts precipitated with hydrogen sulphide yield mixtures of cupric and cuprous sulphide are not correct. The cupric sulphide thus formed is amorphous and of dark green color. When heated in hydrogen sulphide at about 150° it becomes dark blue and probably crystalline.

Weinschenk's[45] method of heating cupric salts in a sealed tube with hydrogen sulphide at about 250° yields well-crystallized cupric sulphide. Covellite was also obtained in this laboratory by Dr. E. G. Zies by the reaction of a ferric alum solution on chalcopyrite in a sealed tube at 200°.[46]

Cupric sulphide is also formed when cuprous sulphide is treated with a dilute acid solution in presence of oxygen. The reaction that takes place may be expressed by the equation:

$$Cu_2S + 2H^{\cdot} + O = CuS + Cu^{\cdot\cdot} + H_2O.$$

When cupric salt solutions are heated with excess of sodium thiosulphate cupric sulphide and sulphur are precipitated.

PHYSICAL PROPERTIES OF CUPRIC SULPHIDE.

The specific gravity of covellite is usually given as 4.59–4.64. Stevanovic[47] more recently obtained the value 4.668 at 13°, which neglecting the small expansion of the mineral would correspond to 4.665 at 4°. It should be mentioned that Stevanovic's value was determined on about 0.6 g. of material, a quantity too small for very high accuracy. We determined the specific gravity of two very pure samples of covellite from Butte, Montana. The analyses were as follows:

[44] Thomsen, *Ber.*, 11, 2043 (1878); Brauner, *Chem. News*, *74*, 99 (1896).
[45] *Zt. f. Kryst.*, *17*, 486 (1890).
[46] Unpublished work.
[47] *Zs. Kryst.*, 44, 349 (1908).

TABLE XVII.

ANALYSES OF COVELLITE FROM BUTTE, MONTANA.

No.	Cu.	S.	Fe.	SiO_2.	Total.
1	66.43	33.28	0.05	0.07	99.83
2	66.46	—	—	—	—

The specific gravities of both samples were higher than any previously given.

TABLE XVIII.

SPECIFIC GRAVITIES OF COVELLITE.

No.	Weight used for Determination g.	Mineral $\frac{25°}{\text{water } 25°}$.	Mineral $\frac{25°}{\text{water } 4°}$, calculated.
1	9.2582	4.696	4.682
1	9.2923	4.698	4.684
2	8.0500	4.691	4.677

We also determined the specific gravity of several of our synthetic cupric sulphide preparations and found them to vary with the fineness of the material used. Thus very finely divided cupric sulphide, obtained by precipitating with hydrogen sulphide and heating to 200° in hydrogen sulphide, had the specific gravity of $4.615 \frac{\text{cupric sulphide } 25°}{\text{water } 25°}$. A coarser crystallized cupric sulphide, made by heating copper wire in sulphur vapor at about 300°, had the specific gravity of $4.651 \frac{\text{cupric sulphide } 25°}{\text{water } 25°}$. Still another, made by heating cuprous sulphide in sulphur vapor in a sealed evacuated tube at about 425°, had the specific gravity of $4.665 \frac{\text{cupric sulphide } 25°}{\text{water } 25°}$. The lower density of the synthetic preparations, as compared with our natural covellite from Butte, Montana, is probably due to occlusion of air by aggregates of very fine crystals.

Cupric sulphide crystallizes in the hexagonal system. In very thin sections it is sufficiently transparent to permit the determination of the refractive index.

MICROSCOPIC CHARACTERISTICS OF COVELLITE.

Crystals of microscopic size only have been obtained by our

laboratory methods. Those produced by dry heating were in dense, radiating aggregates of the characteristic blue color.

Crystals made in solutions attained a maximum diameter of about 0.1 mm., and were always of the same habit, that is, hexagonal plates. A strong tendency toward subparallel groupings was always observed. This led either to the formation of thin skeletal plates or to a compact pile of plates. Single perfect plates have a strictly hexagonal outline as nearly as can be determined by the microscope. Those sufficiently thin are green by transmitted light, dark between crossed nicols, and do not give an interference figure. When tilted, however, they are doubly refracting and pleochroic. One ray vibrates in the plane of the plates. This is more strongly absorbed. These crystallographic and optical characteristics belong only to hexagonal symmetry. The thinness of the plates probably explains the failure to give a uniaxial interference figure. The tendency to form subparallel groups seems entirely sufficient to account for the measurements obtained by Stevanovic[48] from natural crystals, which led to the idea that covellite might not be hexagonal but monoclinic or triclinic. Furthermore, the variation in the only two fundamental angles measured are so great that the calculated angle, β, is not significant. No angle of primary importance in calculating β was observed.

The pleochroism observed in covellite and the differences in color of polished surfaces cut from the mineral in different crystallographic directions have direct relations to the refractive indices and the absorptive power. A study of these and other allied optical phenomena has been recorded already.[49] Sections parallel to the base (cleavage) are much darker blue than those parallel to the vertical axis. The refractive index $\omega_{Tl} < 1.0$, $\omega_{Na} = 1.45$, $\omega_{Tl}^{\infty} = 1.80$. The crystals are optically positive.

THERMAL BEHAVIOR OF CUPRIC SULPHIDE.

Cupric sulphide dissociates at comparatively low temperature and its melting point can not therefore be determined under ordi-

[48] *Loc. cit.*

[49] *Journal Washington Academy of Sciences*, 5, 341 (1915).

uary conditions. The dissociation of cupric sulphide, $4CuS \rightleftarrows 2Cu_2S + S_2$, has been investigated by Preuner and Brockmöller[50] and their results are given in Table XIX., where A is the total sulphur pressure and p the partial pressure of S_2 molecules.

TABLE XIX.

DISSOCIATION OF CUPRIC SULPHIDE—PREUNER AND BROCKMÖLLER.

Temperature.	A in mm.	p in mm.
450	80	14.5
470	200	31
475	250	37
480	313	44
500	980	92

As seen from these data the dissociation of cupric sulphide increases very rapidly with rising temperature.

TRANSFORMATION OF CHALCOCITE IN AN ATMOSPHERE OF HYDROGEN SULPHIDE INTO COVELLITE.

It has been mentioned before that when cuprous sulphide is heated in an atmosphere of hydrogen sulphide its sulphur content increases with the decrease of temperature. As has already been shown, this is due to formation of cupric sulphide, which dissolves in cuprous sulphide (Fig. 78). At 358° (± 5°), in an atmosphere of pure hydrogen sulphide, cuprous sulphide can be changed entirely into cupric sulphide, and above this temperature cupric sulphide loses its sulphur. Table XX. shows that when cupric sulphide was heated in an atmosphere of hydrogen sulphide at 362° it lost part of its sulphur, but gradually regained it again when it was heated at 353°.

TABLE XX.

BEHAVIOR OF CUPRIC SULPHIDE WHEN HEATED IN HYDROGEN SULPHIDE ABOVE AND BELOW 358°.

Time of Heating.	Temperature.	Copper Contents in Per Cent.
5–6 hours	362°	66.75
5–6 hours	353°	66.65
5–6 hours	362°	67.09
5–6 hours	353°	66.90
5–6 hours	353°	66.41

[50] *Z. Phys. Chem.* *81*, 129 (1912).

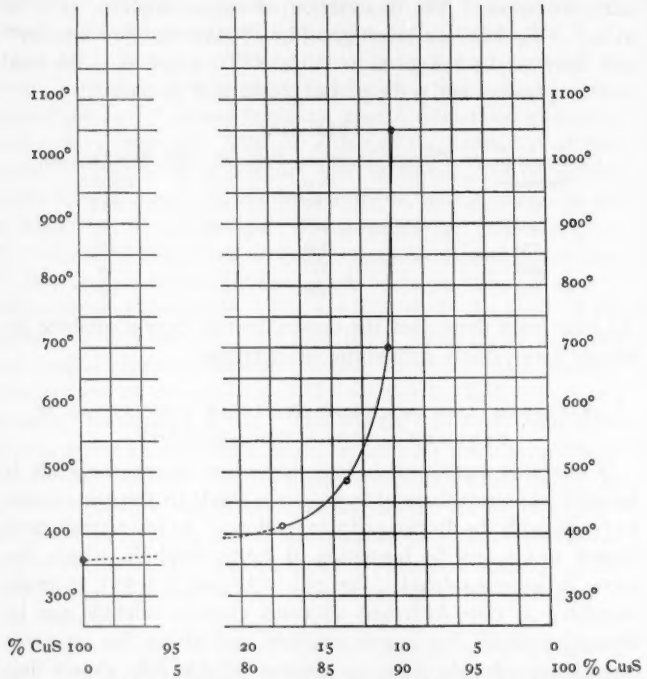

FIG. 78. Showing the composition of copper sulphide when heated in hydrogen sulphide at various temperatures.

At 358° the dissociation pressure of cupric sulphide is in equilibrium with the partial pressures of hydrogen sulphide. Above this temperature[51] the dissociation pressure of cupric sulphide increases very rapidly with rise in temperature; that of hydrogen sulphide only slowly. For that reason cupric sulphide rapidly loses sulphur and forms cuprous sulphide. Part of the cupric

[51] Experiments now in progress in this laboratory indicate that the dissociation pressure of covellite at this temperature is only a fraction of a millimetre of mercury. This work has been delayed by the lack of a sufficiently sensitive quartz glass pressure gauge with which we are planning to repeat Preuner & Brockmöller's measurements.

sulphide dissolves in the cuprous and in that state decomposes but little.

SUMMARY.

1. Cuprous sulphide was prepared in a vacuum furnace and its melting point determined therein; the latter was found to be 1130° ± 1°. No dissociation of cuprous sulphide takes place at 1200°. The specific gravity of synthetic cuprous sulphide, $\frac{\text{substance } 25°}{\text{water } 4°}$, was found to be 5.785; practically the same as the specific gravity of the purest natural mineral which we analyzed, viz. 5.783 $\frac{\text{mineral } 25°}{\text{water } 4°}$.

2. The copper sulphides obtained by fusing together copper and sulphur are of variable composition and always contain more sulphur than the ratio 2Cu : S demands. They are microscopically homogeneous and vary continuously both in color and in specific gravity with composition; as the sulphur increases they become darker in color and lighter in gravity. The specific volumes of these products lie within the limits of error on the straight line connecting the specific volumes of cuprous and cupric sulphide. It has been shown that such products are solid solutions of cuprous and cupric sulphide.

Copper sulphide melts in an atmosphere of hydrogen sulphide at 1096°; in an atmosphere of sulphur vapor at 1057°. The lower melting point as compared with that of cuprous sulphide is due to dissolved cupric sulphide, which increases with the increase of the sulphur vapor pressure surrounding it.

When cuprous sulphide is heated in an atmosphere of hydrogen sulphide at various temperatures (below the melting point), its sulphur content increases. For each temperature the products contain a definite amount of sulphur. This sulphur content increases with the decrease in temperature until at 358° the product becomes cupric sulphide.

Solid solutions of cuprous-cupric sulphide were also prepared by heating compressed powders of the two sulphides at about 100°.

3. The analyses of a number of natural chalcocites from

widely varying localities proved that solid solutions sometimes occur in nature. The geological significance of this fact is yet to be discovered.

4. In connection with the occurrence of solid solutions of the two copper sulphides, the problem of the nature of pyrrhotite has been discussed.

5. Cuprous sulphide is dimorphous. The inversion temperature was found at about 91°. It has been shown that the size of the grains considerably influences the inversion temperature.

6. Increasing amounts of cupric sulphide, dissolved in cuprous sulphide, raise the inversion temperature. This takes place until cupric sulphide reaches the concentration of about 8 per cent., after which an inversion is no longer observed.

7. Crystals of chalcocite were repeatedly formed in the dry way at various temperatures, but only above about 250° were they large enough to allow the determination of their symmetry; all these crystals were isometric.

Isometric crystals of cuprous sulphide were also obtained from solutions: at 250° by the reaction of cuprous chloride with sodium sulphide, and at 200°, 170° and 125° by recrystallization of cuprous sulphide in solutions of hydrogen sulphide.

8. Crystals formed by the action of ammonium sulphide on copper, repeatedly described in the literature as orthorhombic cuprous sulphide, have in reality the composition: $Cu_7(NH_4)S_4$. A crystallographic study showed that they are not orthorhombic, but tetragonal.

9. Observation of cleavage and parting, combined with a knowledge of the effect of dissolved cupric sulphide on the inversion of cuprous sulphide are applied to the problem of distinguishing primary from secondary chalcocite ores.

10. Covellite has been prepared in many different ways and a crystallographic and optical study of it made. It is hexagonal, optically positive; the optical dispersion of ω is extremely high, $\omega_{Li} < 1.0$, $\omega_{Na} = 1.45$, $\omega_{Tl} = 1.80$.

The specific gravity of two very pure samples of natural covellite has been determined and found to be 4.683 and 4.676 respectively $\left(\frac{\text{mineral } 25°}{\text{water } 4°}\right)$. This specific gravity is higher than any

previously given. The specific gravity of synthetic covellite varied with the fineness of the material used. This was probably due to occlusion of air by aggregates of very fine crystals. The highest value obtained with synthetic covellite was 4.652 $\left(\frac{\text{substance } 25^\circ}{\text{water } 4^\circ}\right)$.

Covellite can be heated in an atmosphere of hydrogen sulphide up to 358°; this is the temperature at which covellite is in equilibrium with the gas, and at this temperature and below it chalcocite can be completely converted into covellite.

The authors wish to extend their thanks to Professors Dana and Ford of Yale University, Professors Palache of Harvard, Moses of Columbia, A. F. Rogers of Leland Stanford, Drs. George P. Merrill and Edgar Wherry of the National Museum, and Professor Brögger of Christiania for the kindly way in which they have aided this work by furnishing us with many mineral specimens.

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CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., APRIL 24, 1915.

CERTAIN MINERAL OCCURRENCES IN THE WORTHINGTON MINE, SUDBURY, ONTARIO, AND THEIR SIGNIFICANCE.

T. L. WALKER.

The Sudbury copper-nickel ore bodies, as is well known, occur in connection with basic igneous rocks. The rock in the fresh form is norite, but frequently it is so altered that it can be best described as epidiorite or diorite. The ore bodies commonly occur on the basic border of the eruptive which becomes more acid and lighter in color as the distance from the ore bearing border is increased. This transition from basic at one border to acid at the other border of the nickel bearing eruptive was first pointed out by the writer[1] who attributed the variation to magmatic differentiation. The later workers on the geology of the Sudbury region have generally approved this interpretation and have usually claimed that the ore bodies are due to magmatic differentiation.[2] Since the chief nickel mineral is nickeliferous pyrrhotite, the copper-nickel ore is referred to as pyrrhotite norite.

The chief mass of nickel-bearing norite forms a continuous band bordering a great ellipse, 35 miles long and 15 miles across. In width this eruptive varies from two to four miles, the outer part of the band being basic and frequently marked by important ore bodies, while the inner part is acid and devoid of such deposits. The central part of this great ellipse is occupied by pre-Cambrian sedimentary rocks. The whole complex forms a great syncline, the lowest member being the nickel eruptive which Coleman regards as a great intrusive sheet.

Apart from the main nickel bearing eruptive just referred to there are several more or less irregular masses of the same petro-

[1] T. L. Walker, *Quart. Journ. Geol. Soc.*, Vol. LIII. (1897), p. 40.

[2] Coleman, A. P., "The Nickel Industry," Mines Branch, Ottawa, 1913 Barlow, A. E., "Nickel and Copper Deposits of Sudbury, Ontario," Geol. Survey of Canada, Ottawa, 1901.

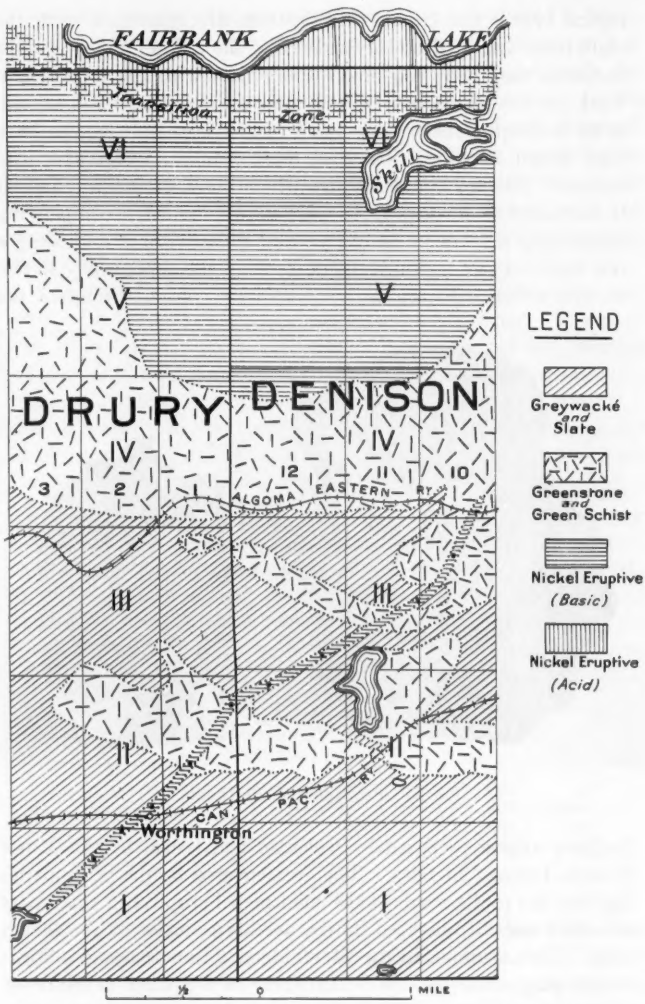


FIG. 79. Geological map of the Worthington Mine and Vicinity.

logical type. Sometimes these masses are connected with the main mass and project outwards from the ellipse, while in other instances they show no direct connection with the large mass. They are sometimes only a few hundred feet across and several miles in length. Some important nickel-copper ore bodies have been found in connection with these smaller, irregular norite masses. The igneous mass with which the Worthington deposit is connected is of this type. As shown on the accompanying sketch map it attains a length of four miles without exceeding a few hundred feet in width. The geology and topography shown on this sketch map are derived from the excellent map of the

FIG. 80. Pentlandite in Pyrrhotite.

Sudbury region prepared by Coleman and issued by the Mines Branch, Ottawa, in 1913. The area covered by the accompanying map lies to the south of the chief nickel eruptive, a small part of which may be observed on the northern border of the sketch map. The ore mined at the Worthington Mine occurs in a hornblende plagioclase rock in which there is abundant evidence of alteration. In some of the nickel mines of the region fresh norite

occurs but generally the pyroxene is more or less altered to hornblende. Owing to the presence of all stages in the alteration it is reasonable to conclude that the epidiorite associated with the nickel ores results from the uralitization of pyroxene. In the case of the Worthington ore this is the chief type of rock observed.

The sulphides prominent in the Worthington ore are pyrrhotite and chalcopyrite, through which are scattered pentlandite in the form of lustrous cleavable phenocrysts of a pale, brassy color and nickeliferous pyrite with subordinate amounts of polydymite and rarely sphalerite, niccolite and molybdenite.

The masses of pentlandite vary in size from particles to be seen only with the lens to masses two inches in diameter. It was in ore from this mine that the writer first recognized the presence of pentlandite in the Sudbury ores. In the Worthington Mine the pentlandite is most abundant in the pyrrhotite (Fig. 80) but it is also frequent in the chalcopyrite and pyrite. In the other nickel deposits of the district the pentlandite particles are usually microscopic in size. It is now generally maintained that the nickel values of the pyrrhotite are due to the presence of small particles of pentlandite scattered through the pyrrhotite rather than to the isomorphous replacement of iron by nickel. In the Worthington Mine the pentlandite is exceptional in that the individual masses of the mineral are macroscopic in size. The octahedral cleavage of the pentlandite is such that a fragment examined on the reflecting goniometer gives good reflections for the various octahedral surfaces. A chemical analysis of some of the purest pentlandite gave the following result:

	Per Cent.			
Fe	30.68	÷ 55.9	= .5495	1.1582
Ni	34.48	÷ 58.7	= .5870	
Co	1.28	÷ 59	= .0217	
S	32.74	÷ 32.06	= 1.0212	
Insoluble	.56			
	99.74			

From this analysis it should be observed that the bases are present in proportions too large for the chemical formula [Ni, Fe]S usually given for this mineral. This was first observed by Dickson[3] who suggested that according to a great many analyses made by him the composition was nearer to $[Ni, Fe]_{11}S_{10}$.

An unusual type of ore found at the Worthington Mine consists of massive pyrite containing rounded masses of pentlandite (Fig. 81) The ore has a conglomeratic appearance and is so abnormal for the Sudbury region as to merit further consideration. The mineral composing the nodules is somewhat dis-

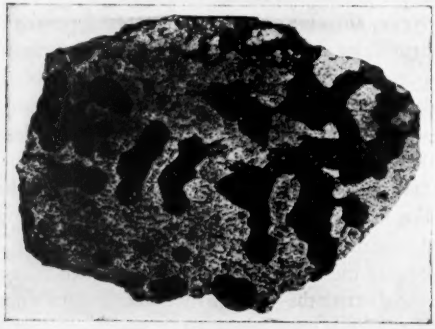


FIG. 81. Pentlandite in Pyrite.

sected by veinlets and stringers composed of ferruginous calcite, while the outermost zone of the nodule is darker in color and weathers very quickly when exposed a few weeks to the air, giving rise to sulphates and in this way suggesting polydymite. It is slightly darker in color and not so lustrous as is usually the case with pentlandite, while the cleavage is rudely cubic, rather than octahedral. A chemical analysis of a sample from one of the purest nodules, (S. G. 4.638) gave the following result:

	Per Cent.
Fe	27.64
Ni	32.13
Co.	.90
Cu	.30
S	34.82
CaO	1.58
Insoluble	.78
	98.15

After deducting the iron and sulphur required to combine with

[3] Dickson, C. W., *Trans. Am. Inst. Mining Eng.*, 1903.

the copper to form chalcopyrite the atomic ratios of the four chief constituents are as follows:

Fe	.490	1.052
Ni	.547	
Co	.015	
S	1.075	

Accepting Dickson's formula for pentlandite $[Fe, Ni]_{11}S_{10}$ it would appear that this nodular material is pentlandite with a small amount of polydymite. The deficiency shown in this analysis is probably due to undetermined magnesia and carbon

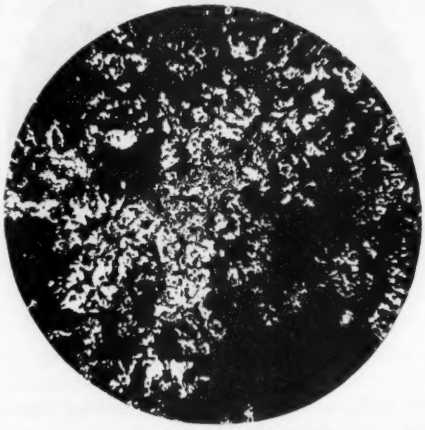


FIG. 82. Calcite and Pyrite, × 40.

dioxide. In view of the preceding observations the writer is inclined to believe that these nodules are largely composed of pentlandite pseudomorphous after polydymite.

The pyrite is light in color and when acted upon by dilute acid betrays the presence of a considerable amount of carbonate. Thin sections of the pyrite mass show that it is quite porous, being composed in part of solid compact pyrite in part of strings of tiny pyrite crystals cemented by calcite (Fig. 82) or quartz (Fig. 83). Throughout the pyrite mass there is also a very small amount of chalcopyrite. The pyrite upon analysis gave the following result:

	Per Cent.			
Fe	44.57 ÷ 55.9	=	.797	.839
Ni	2.44 ÷ 58.7	=	.042	
S	51.83 ÷ 32.06	=	1.617	
	98.84			

The carbonates, the constituents of which were not determined, probably account for the deficiency in this analysis. The atomic ratios show that the mineral is too basic for pyrite. It is probably

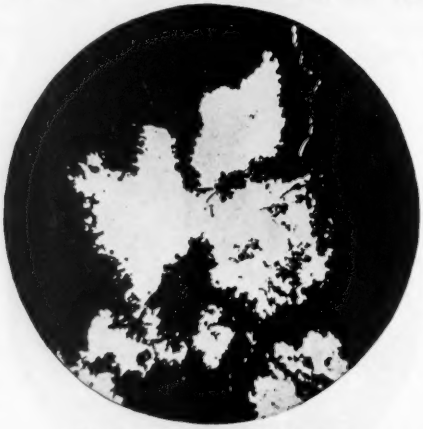


FIG. 83. Quartz and Pyrite, × 40.

a mixture of pyrite and pentlandite. A similar mineral was reported by the writer from the Murray Mine in 1894.[4]

The type of ore here described is exceptional for the Sudbury nickel deposits. It is difficult to avoid the conclusion that the ores as they are now found at the Worthington Mine have been subject to rearrangement by aqueous agencies since the solidification of the rock and sulphides from the original magma. The writer believes it important to emphasize the fact that it is now generally admitted that magmatic segregation *alone* will not account for *all* the phenomena observed by the students of the Sudbury ore bodies.

[4] Walker, T. L., *Am. Journ. Sci.*, April, 1894.

UNIVERSITY OF TORONTO,
TORONTO, ONTARIO, June 25, 1915.

THE ORIGIN OF THE SULPHUR DEPOSITS OF SICILY.

WALTER F. HUNT

INTRODUCTION.

The occurrence and associates of sulphur in nature are so varied that difficulty is frequently encountered in determining the exact manner of their formation. In some instances, the agencies which appear to have been unusually active in one locality, cannot be shown positively to have played even a minor rôle in another district. It is evident, that general methods do not apply equally well to all deposits, but that rather each district must be considered as an individual unit and its geological and structural features thoroughly studied before some intelligent conception may be gained as to the probable origin of the sulphur in that particular locality.

GENERAL TYPES OF SULPHUR DEPOSITS.

Depending upon general methods of formation and occurrence, economic geologists and mineralogists are accustomed to differentiate four distinct types of sulphur: (*a*) metallic sulphide, (*b*) solfatara, (*c*) mineral spring, and (*d*) sulphate.

Metallic Sulphide Type.—It has frequently been observed that the decomposition of metallic sulphides, especially pyrite, marcasite, galena, sphalerite, and stibnite, have produced thin crusts of sulphur, either in a pulverulent form or as masses of small aggregated crystals, which fill the crevices of the rock or line the walls of small geodes. This type is merely of mineralogical interest, as the thin layers of sulphur which result rarely exceed a few inches in thickness.

Solfatara Type.—Issuing from a volcano simultaneously with certain gases, are numerous substances, which, although gaseous at high temperatures, are deposited in a solid form upon cooling.

Among these substances, which are known as sublimates, sulphur is one of the most conspicuous. However, the sulphur thus formed cannot always be distinguished from that produced by secondary changes, namely from the interaction of liberated gases. Most of the analyses of the gases given off from either active or extinct volcanic vents reveal varying amounts of either H_2S or SO_2. From the H_2S thus given off, sulphur may be formed by incomplete oxidation according to the equation: $2H_2S + O_2 = 2H_2O + 2S$. The formation of sulphur in solfatara regions was formerly considered to be due largely to a reaction between H_2S and SO_2, whereby water and free sulphur were formed. This reaction, while taking place readily in the laboratory, has been shown by A. Brun[1] to be practically impossible in nature. Also, in a consideration of the agencies operating in solfataric regions, reference should be made to the experiments of C. Geitner,[2] and of E. Jungfleisch and L. Brunel.[3] These investigators have shown that SO_2 and water vapor react out of contact with air even at ordinary temperatures, the action being accelerated by heat and concentration of SO_2. Above 160° C. sulphur and sulphuric acid are produced according to the following reaction:

$$2H_2O + 3SO_2 = 2H_2SO_4 + S.$$

Below 160° C., $H_2S_2O_4$ is formed as an intermediate product which, upon heating or standing, breaks down to S and H_2SO_4.

Mineral Spring Type.—Sulphur deposits are also quite common around mineral springs, where, by the action of oxygen from the air upon the aqueous solution of H_2S, the sulphur is slowly displaced and appears usually in the form of a fine whitish powder. The mineral associates of this type are usually some form of $CaCO_3$, as limestone, calcite, aragonite, or travertine, and gypsum. However, the chemistry involved in the deposition of sulphur from mineral springs is not quite as simple as that just indicated. More involved changes are also taking place which cannot be so easily traced step by step, but which con-

[1] *Chem. Zeitung*, No. 15, p. 127, 1909.
[2] *Ann. der Chem. u. Pharm.*, Vol. 129, p. 350, 1864.
[3] *Compt. rend.*, Vol. 156, p. 1719, 1913.

tribute toward producing the sulphur and associated minerals mentioned. A. Bechamp[4] has shown that when H_2S is passed into water containing suspended $CaCO_3$, the CO_2 is replaced and two soluble calcium compounds are formed:

$$2CaCO_3 + 2H_2S = Ca(SH)_2 + H_2Ca(CO_3)_2.$$

C. Palmer[5] has shown that the sodium and potassium salts, which are always present in mineral springs, increase this solvent action of a hydrogen sulphide water on calcium carbonate. The calcium hydrosulphide formed will, upon the escape of the H_2S, deposit gypsum, or calcite or aragonite according to the following reactions:

$$Ca(SH)_2 + 2O_2 + 2H_2O = CaSO_4.2H_2O + H_2S$$
$$Ca(SH)_2 + CO_2 + H_2O = CaCO_3 + H_2S.$$

Another force which is usually active in the mineral spring type is the rôle played by small organisms that live and thrive in sulphureted water, and that S. Winogradsky[6] has named sulphur bacteria. These organisms possess the power of oxidizing H_2S to H_2SO_4, and of storing free sulphur in their cells when an excess of this gas is present. The H_2SO_4 so formed attacks in turn the calcium bicarbonate taken into the cell from the water, and returns it to the medium in the form of calcium sulphate. Still other reactions might be mentioned in connection with the mineral spring type. Soluble polysulphides and thiosulphates, which often accompany the sulphides in natural waters, are decomposed by CO_2 with the liberation of H_2S and S. Finally, Raffo and Marncini[7] have shown that colloidal sulphur can be carried in solution, and that a solution is stable which contains S, H_2SO_4, and Na_2SO_4 in the following proportions: S (colloidal) 2.79–2.60 per cent., H_2SO_4 6.43–7.00 per cent., and Na_2SO_4 3.75–3.92 per cent. Any change in the concentration of the salt will cause a precipitation of the sulphur. It will thus be seen that many factors are operative in the mineral spring

[4] *Ann. chim. phys.*, 4th ser., Vol. 16, p. 234, 1869.
[5] Bull. U. S. Geol. Surv., No. 340, p. 455, 1908.
[6] *Botanische Zeit.*, Vol. 45, Nos. 31–37, 1887.
[7] *Zeitschr. Chemie Ind. Kolloide*, Vol. 9, p. 58, 1911.

type, each one contributing either directly or indirectly to the production of sulphur and the associated minerals.

Sulphate Type.—Sulphur is commonly found intimately mixed with, or in the vicinity of, bituminous gypsum, which in turn is associated with other sedimentary rocks. It is usually assumed that the bituminous matter of the gypsum causes a reduction of the sulphate of calcium to the sulphide with the production of CO_2 and H_2O. The resulting sulphide is then further decomposed by CO_2, H_2O, and O_2, yielding calcium carbonate and sulphur. Sulphates are, however, very stable compounds and their reduction at ordinary temperature by lifeless organic material is to be seriously questioned. On the other hand, it has been known for some time to bacteriologists that certain living micro-organisms are capable, under certain favorable conditions, of reducing sulphates in solution with the liberation of hydrogen sulphide. This important biochemical reaction has been only recently alluded to in geological literature[8] and then but briefly.

OBJECT OF THIS INVESTIGATION.

The sulphur deposits of Sicily occupy the south-central portion of the island and are distributed over an area extending from Centuripe in the east to Gibellina in the west, approximately 160–170 km. in an east-west direction, then south to the coast, with a maximum width of about 90 km. The sulphur bearing stratum is not continuous over this entire area but is restricted to isolated, basin-like deposits. After the deposition of the sedimentary rocks with their disseminated sulphur, violent terrestrial movements have broken and tilted the layers leaving some of them in an almost vertical position (see Fig. 94). Subsequent erosion of these disturbed earth blocks has not only, in some instances, made it extremely difficult to correlate corresponding strata in even adjoining districts, but has destroyed some of the deposits as well, so that it is extremely probable that the sulphur area was more extensive in earlier geological periods than at present. In other places, the sulphur bearing layers are still con-

[8] O. Stutzer, "Die Wichtigsten Lagerstätten der Nicht-Erze," Vol. I, p. 259, 1911.

cealed by more recent sedimentary deposits. The mines are concentrated in groups where the ore is richest and the expense of extraction least (see Fig. 84).

With reference to the origin of these sulphur deposits, numerous and diverse theories have been at various times proposed by different investigators. Some have argued for an explanation

FIG. 84. Map of Sicily showing location and relative productive importance of sulphur mines. Scale 1 : 3,000,000. (After Baldacci.)

based on solfataric action, others were firmly convinced that these deposits were typical mineral spring types, while still others have endeavored to utilize the gypsum in an attempt to explain these enormous, although not exceedingly rich, deposits, which have been worked more or less continuously for the past three centuries.

Within recent years, the research work carried on along biological-chemical lines has been extremely fruitful, and the mineralogist and geologist have, at present, at their disposal a much

larger fund of information than was available when the majority of these theories were proposed. In view of the many conflicting theories which have been advanced, the rather early date of many of them, and the strides of science latterly, a reëxamination was considered very desirable. It was in an endeavor to explain these sulphur deposits in the light of modern biological-chemical reactions and under normal conditions, especially with reference to temperature, that this investigation was undertaken.

GEOLOGY OF THE SULPHUR DISTRICTS OF SICILY.

Before taking up the origin of the sulphur deposits, with which we are more especially concerned, we must consider very briefly the main geological strata of that section of the island of Sicily in which the sulphur mines occur. For the interpretation of the geology of this exceedingly complex region we are largely indebted to S. Mottura[9] and L. Baldacci,[10] whose memoirs are always quoted on works dealing with Sicilian sulphur. Stelzner-Bergeat[11] and O. Stutzer[12] have rendered the data of these noted Italians more accessible by their clear, summarized accounts in German.[13]

The succession of the formations here given cannot be considered absolutely constant in all sections of the sulphur-bearing district. In some places one or even several members of the series may be entirely lacking, while in other places the order

[9] "Sulla formazione tertiaria nella zona solfifera della Sicilia," *Memoire R. comitato geologico d'Italia*, Vol. 1, 1871; reprinted: Caltanissetta, 1910, edito a cura della Societa dei Licenziati della R. Scuola Mineraria di Caltanissetta.

[10] Descrizione geologica dell' Isola di Sicilia," *Memorie descrittive della Carta geologica d'Italia*, Vol. 1, Rome, 1886.

[11] "Die Erzlagerstätten," Vol. 1, p. 457, 1904.

[12] "Die Wichtigsten Lagerstätten der Nicht-erze," Vol. 1, p. 197, 1911.

[13] See also: G. von Rath, *Neues Jahrb. f. Min. Geol. und Pal.*, pp. 584–603, 1873; Ch. Ledoux, *Annales des mines*, (7), 7, pp. 1–84, 1875; A. V. Lasaulx, *Neues Jahrb. f. Min., Geol. und Pal.*, pp. 490–517, 1879; E. Stoehr, "Notizie preliminari su le piante ed insetti fossili della zona solfifera della Sicilia," *Boll. R. Com. geol.*, No. 9–10, 1875; Ref. *Neues Jahrb.*, p. 321, 1877; *Neues Jahrb.*, pp. 169–171, 1874.

may vary slightly from that given below which might be considered, however, as the normal sequence, especially in the south-central portion of the Island.

UPPER PLIOCENE.

Yellow Sands and Sandstones.—In the sulphur bearing section the youngest formation which is usually encountered is that of the yellow sands of the Upper Pliocene. The sands are more or less cemented, the binding material being in some cases calcium carbonate, and in others, silicious material. These sands contain numerous marine fossils and may reach a maximum development of over one hundred meters.

Shell Breccia.—Below the yellow sands and sandstones is a formation known as the shell breccia (tufo calcareo o breccia conchigliare). It is a limestone formation of an earthy yellow color, abounding in fragments of fossil shells. The thickness of this formation varies considerably, from a few meters to over one hundred meters. The shell breccia rests in turn upon *blue clays,* which also contain marine fossils. This series, from the blue clays at the bottom to the yellow sands at the top, is usually nearly horizontal, with a slight dip to the south. It rests almost always unconformably upon the Lower Pliocene. Fig. 85 illus-

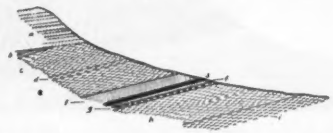


FIG. 85. Profile of strata near Caltanisetta. (After Ledoux.)

a = sandstones, 100 meters; *b* = shell breccia, 100 meters; *c* = blue clay, 60 meters; *d* = foraminiferous marls, 10 meters; *e* = gray clay, 60 meters; *f* = gypsum and clay, 25 meters; *S* = sulphur ore, 4 meters; *g* = calcareous tripoli, 5 meters; *h* = saliferous clay, 80 meters; *i* = gray clay, 200 meters.
Scale 1 : 15,000.

trates only in a general manner the succession and thicknesses of the various strata near Caltanissetta. The profile, however, does not reveal the unconformity at the close of the Lower Pliocene.

LOWER PLIOCENE.

Foraminiferous Limestone.—This formation is also known as the "trubi" and has a variable composition, passing from an impure clay to a true limestone. It is stratified and conformable with the underlying gypsum-sulphur formation, and from this fact it might be inferred to belong to the same period as the latter (upper Miocene), but the fauna, according to Baldacci, is decidedly Pliocene in character. It has a maximum thickness of 150 meters. In some localities beds of clay are found between these limestones and the gypsum underneath (see Figs. 2 and 10).

UPPER MIOCENE.

The Gypsum-sulphur Formation[14] (*Serie gessoso-solfifera*).—This formation is by far the most important, commercially, of the entire geological series, as it is in this series of rocks that the deposits of sulphur are located. They rest directly upon the tripoli and generally in perfect conformity, indicating that the formations succeeded one another without any violent terrestrial

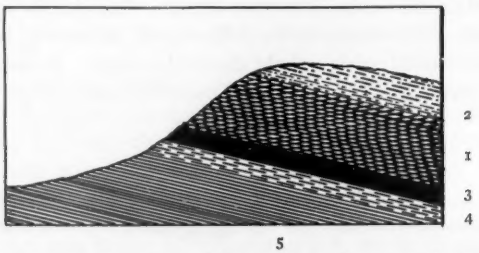


FIG. 86. Cross-section of a sulphur mine southeast of Castrogiovanni. (After Mottura.) The gypsum-sulphur formation rests conformably upon the tripoli. 1 = Foraminiferous limestone (or "Trubi"); 2 = Gypsum; 3 = Sulphur rock; 4 = Tripoli; 5 = Marl.

Scale 1 : 1500.

disturbances. Fig. 86, representing a cross section of a sulphur mine southeast of Castrogiovanni, illustrates this conformity.

[14] E. Kayser places this formation in the Lower Pliocene. "Lehrb. d. Geol." Part 2 (Formationskunde), 3d ed., p. 592, 1908.

The gypsum, which comprises the upper member of the gypsum-sulphur series, is very extensive, in its horizontal as well as in its vertical extent. It covers an area of over 800 sq. km., and possesses in a number of places a thickness of over 100 meters. It not only conceals the true sulphur bearing rock beneath, but extends into areas in which the sulphur is entirely absent. The fossils that have been found in the gypsum, while not very abundant, indicate, however, marine conditions.

Sometimes the sulphur is found in small, irregular, lens-shaped masses scattered through the gypsum. When thus found it is very pure, but so limited in extent that it is mined only when it is in the proximity of the true sulphur beds. The beds or zones which contain the sulphur of economic importance occur in al-

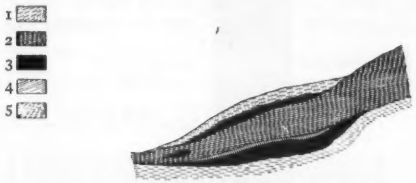


FIG. 87. Mine Zubi (San Cataldo). Sulphur beds near the top as well as the bottom of the gypsum formation. 1 = Foraminiferous limestone (or "Trubi"); 2 = Gypsum; 3 = Sulphur rock; 4 = Calcareous or Sandy gypsum; 5 = Tripoli.

Scale 1: 8,000.

most every case toward the base of the gypsum formation. At times, however, a sulphur zone is found near the top as well as near the bottom of the gypsum, as is seen in Fig. 87, which represents a vertical section of a mine near San Cataldo and for which I am indebted to Mr. A. G. Oliveri.

The individual sulphur beds vary in thickness from one meter to, in rare instances, almost thirty meters. Generally in a given locality three or four beds are encountered, one above the other, separated from each other by narrow, sterile layers of bituminous, salty clays and shales (tufi). These sterile intercalations rarely exceed one meter in thickness. A cross section of one of the mines at Sommatino, Solfara Grande, Fig. 88, reveals six

independent beds varying in thickness from 2 to 8.5 meters and possessing an aggregate thickness of over 30 meters. The sulphur content in beds 2 and 12 averages 18 per cent.; in beds 4 and 10, 22 per cent.; and in 6 and 8 about 26 per cent. The bituminous, and more or less salty shales (tufi) which separate the various sulphur beds are also found interspersed through the gypsum above. The distribution of the sulphur zones and their relation to the gypsum-sulphur formation can, perhaps, be best

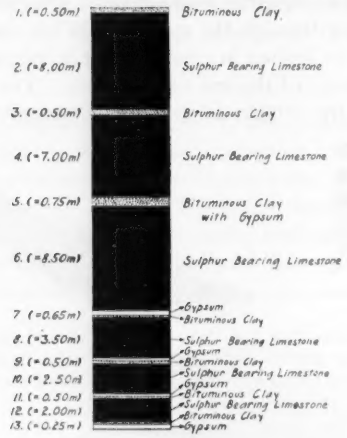


FIG. 88. Cross-section of *Solfara Grande di Sommatino*. (After Mottura.) Scale 1 : 500.

illustrated by a more detailed account of a few typical localities.

Numerous sulphur mines are to be found in the vicinity of Racalmuto and Grotte. Best known are those of Mount Cimicia and Pernice-Cannatone. With the exception of small, isolated lenses of sulphur scattered here and there through the gypsum, the occurrence at Mt. Pernice consists of two rich zones. The upper (stagnone) lies between the gypsum and "trubi." It has an average thickness of 10 m. with a sulphur content of 30 per cent. and dips 25° E.S.E. Below this zone is a massive bed of gypsum (127 m.) with interbedded shales. Below this bed of

gypsum a 1.30 m. layer of bituminous shale is found with a small amount of sulphur, and then the second sulphur zone is encountered, which is separated into beds by "tufi." Here the dip varies from 35–40° SE. and the sulphur content from 15–25 per cent. Then follows the customary silicious limestone and finally the tripoli.

On Mt. Cimicia we find the Giona, Mendola, and Cozzo Tondo mines. Here the sulphur bearing bed varies from 2–3.5 m. and the sulphur from 18–20 per cent. Characteristic of these mines is the impregnation of the sulphur zone with an unusually large amount of bituminous matter. As a result, the crude sulphur is dark colored, containing 6–8 per cent. bitumen.

Near Racalmuto are to be found the Tulumello, Bordonaro, and Alfano mines. Here the sulphur bearing zone is about 4 m. in thickness and extends for about 250 m. in an E-W direction. The sulphur content varies from 20–23 per cent. and the rocks have a dip from 65–70° to the south. Another important group of mines is to be found near Naro, consisting of Virdilio, Min-

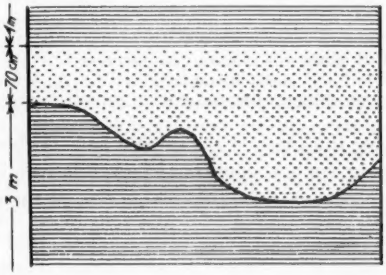


FIG. 89. Shale unconformable with lower sulphur bed. (After Stutzer.)

tina and Mintinella. The sulphur bed, which in this district is about 15 m. in thickness, is overlain by "trubi" and underlain by silicious limestone. The dip is 25° to the south and the average sulphur content is approximately 50 per cent., reaching, however, in isolated places as high as 80–90 per cent.

Some of the most productive mines of the entire Island are located in the vicinity of Caltanissetta. One of the main pro-

ducers in this section is the Trabonella. Here the dip measures 30° to the south, but not far distant it is increased to 52°. The aggregate thickness of the sulphur bearing strata reaches 22 m., while the sulphur averages 18 per cent. At the Gessolungo-Trigona Mine, located also near Caltanissetta the sulphur occurs in two beds separated by bituminous shale and limestone. It was at this mine that O. Stutzer reported a cross bedding of the limestone and sulphur bearing strata with erosion of the lower sulphur bed before the deposition of the over-lying shale. The second sulphur bed, however, lies conformably upon the shale (see Fig. 89).

Near Sommatino the following mines are to be found: Solfara Grande, Solfarella di Sommatino, and Solfara del Fiume de Riesi. The occurrence of the sulphur at the Solfara Grande di Sommatino has already been referred to. At the Solfarella di Sommatino we observe the following cross section:

	Meters.
Sulphur bed of varying thickness	
Bituminous shales	40.00
Sulphur bed ("Vanella bianca")	6.00
Bituminous shale	0.50
Sulphur bed ("Vanella soriata")	5.00
Bituminous shale	0.50
Sulphur bed ("Vanella bastarda")	6.00
Tripoli and silicious limestone	12–20

The aggregate thickness of the sulphur beds is about 20 meters while the sulphur content appears to be in the vicinity of 31 per cent. It is apparent that the sulphur content of the sulphur rock is far from constant and that it varies greatly. This fact is illustrated by the following table:

	Per Cent.
Montedoro	13–25
Pernice at Racalmuto	30
Muculufa	17–18
Naro	50
Licata	15
Juncio Group at Caltanissetta	20–22
Trabonella	18
Madore (Lercara)	20
Grottacalda (Valguarnera)	25–27
Sommatino	18–26
Cimicia (Racalmuto)	21

In the above descriptions reference has been made to the sulphur bed or zone, but nothing has been said as to the nature or occurrence of the sulphur in these beds. The sulphur occurs disseminated throughout the limestone, which, in some instances, is rather cellular, and again, quite compact. The limestone, grayish, brownish or light yellow in color, is more or less impure from admixture of clay, gypsum, or bituminous matter. At intervals thin seams or bands of pure sulphur, from 5 mm. to 2 cm. in thickness, are seen extending parallel to the bedding (see Fig. 90). Frequently small pockets and veins of secondary sulphur

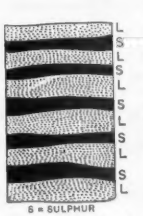


FIG. 90.

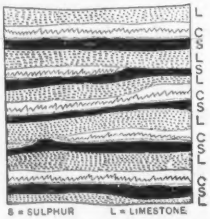


FIG. 91.

FIGS. 90 and 91. Diagrammatic sketches, illustrating occurrence of sulphur in limestone. (After Mottura.)

occur which cut through the limestone without any regularity. At times above the sulphur seams are open spaces which permit crystals of secondary calcite to attach themselves to the hanging wall with their sharp points projecting downward (Fig. 91). The walls of small geodes and fissures in the limestone are often completely covered with beautiful crystals of sulphur, calcite, aragonite, gypsum, celestite, barite, quartz and melanophlogite.

Considering the lens or basin-like character of the sulphur formation, the large number of deposits, their independence and their small extent, Mottura suggested that deposition must have taken place in restricted basins or lagoons. Near Villarosa, the sulphur formation has a length of approximately 7 km.; at Caltanissetta, not over 5–6 km.; at San Cataldo, less than 2 km.; and at Grottacalda, 3.5–4 km. The width of the formation varies from 300 m. to 1 km. An average would probably approximate 500 m. Through the courtesy of Mr. A. G. Oliveri, the follow-

ing sketches were obtained, illustrating the character of the sulphur formation at the Aronica, Severino, Bosco and Stincone mines (Figs. 92 and 93).

Below the gypsum-sulphur formation there often occurs a

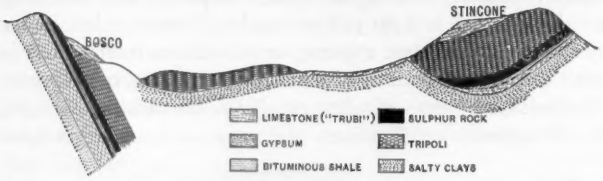


FIG. 92. Character of sulphur formation at Bosco and Stincone mines (Serradifalco).
Scale 1 : 12,000.

compact limestone which at its base becomes silicious and grades into the underlying tripoli. Its thickness is occasionally 50–60 meters, but usually only 1–3 meters.

Tripoli.—This deposit reaches a maximum development at Racalmuto, where it is 150 meters in thickness. Generally, how-

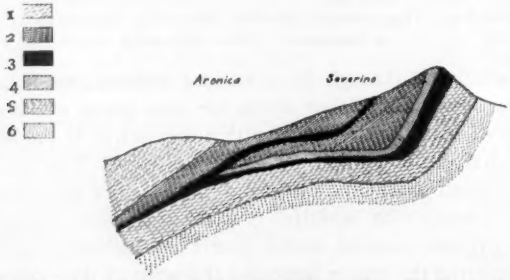
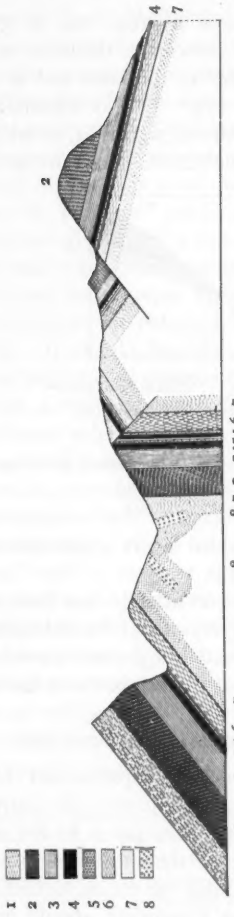


FIG. 93. Mines Aronica-Severino (Castrogiovanni). Character of the Sulphur formation at Aronica and Severino mines. 1 = Foraminiferous Limestone (or "Trubi"); 2 = Gypsum; 3 = Sulphur Rock; 4 = Calcareous or Sandy Gypsum; 5 = Tripoli; 6 = Clays, Salty and Bituminous.
Scale 1 : 8000.

ever, it does not exceed 60 m. and frequently is only 2–3 m. thick. Its color varies from white or gray to a dark brown. It has a loose and mealy texture and consists largely of fragments of



1 = Limestone ("Trubi"); 2 = Gypsum; 3 = Bituminous Clay or Shale; 4 = Sulphur Rock; 5 = Siliceous Limestone; 6 = Tripoli; 7 = Salty Clays; 8 = Salt.

FIG. 94. Cross-section near Racalmuto, illustrating salt deposits in the salty clays below the tripoli, as well as the disturbed character of the strata. (After Oliveri.)
Scale 1 : 15,000.

radiolaria, diatoms and sponges. This formation contains a considerable number of fossil fish, insects, plant remains, and and occasionally some lignite.

Salty, Arenaceous Clays.—Finally, below the tripoli, lie salty,

arenaceous clays that contain a great deal of gypsum. This formation may reach the enormous thickness of over 1,000 meters. The clays are salty to the taste and at times contain lenticular masses of pure salt. This is especially true in the vicinity of Racalmuto and Grotte, figure 94, as well as farther to the northwest, between Casteltermini and Cammerata (Fig. 95).

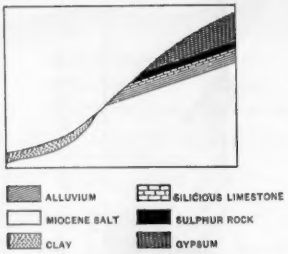


FIG. 95. Sulphur and salt deposits at the Antinori mine near Casteltermini. (After Mottura.)
Scale 1 : 18,000.

These clays contain interbedded layers which are rich in bituminous material and petroleum.

In the above descriptions no attempt has been made to treat exhaustively the geology of any one of the individual regions, as the main object of incorporating a general survey of the strata is to render the discussion of the origin more intelligible.

ORIGIN OF THE SULPHUR DEPOSITS.

With the above discussion of the sequence and character of the formations in the sulphur-bearing districts, the distribution of the sulphur in the limestone and its relation to the accompanying gypsum in mind, the origin of the sulphur may be more easily discussed. It is but natural that the mines, located as they are in a region easily accessible to Europeans, should have been frequently visited and that numerous theories should have been advanced concerning them.

The earlier theories are of sufficient interest to warrant a brief survey.

Earlier Theories.[15]—F. Hoffmann[16] seems to have been one of the first to hazard an opinion upon the origin of the sulphur. He considered it the result of volcanic activity, formed in the same manner as that found at the Solfatara Pozzuoli near Naples, or that produced on the Islands of the Lipari. According to M. Maravigna[17] the sulphur is the result of the decomposition of H_2S dissolved in water which likewise carried marls in suspension. A. Paillette[18] and G. Bischof[19] noted the association of bituminous gypsum with the sulphur and concluded that the latter was due to the decomposition of H_2S, produced by the action of CO_2 and water vapor upon CaS, the origin of which should be attributed to the reduction of gypsum by means of organic material. It should here be noted that although water heated to a temperature of approximately 44° C. is sufficient to decompose CaS, a temperature approaching 700° C. is required for the reduction of calcium sulphate by carbonaceous material,[20] a temperature entirely inconsistent with the existence of the associated minerals, especially gypsum. Not a single feature is present in the sulphur beds to warrant an explanation involving elevated temperatures.

S. Mottura,[21] who in the year 1871 published the first of his comprehensive memoirs, interpreted the beds of tripoli, as well as the sulphur-bearing limestone with its associated gypsum, as lacustrine and not marine deposits. He was led to this belief by the number, independence, small extent, and structure of the sulphur beds, as well as by the presence, especially in the lower horizons, of some fossils of fresh-water fish. These fresh or

[15] Some of the earlier theories will be found in Baldacci's Monograph, p. 331.

[16] Karsten's und von Dechen's Archiv, Vol. 13.

[17] *Compt. rend.*, Vol. 7, p. 304, 1838.

[18] *Compt. read.*, Vol. 16, p. 988, 1843.

[19] Bischof claims priority with reference to the reduction theory, *Chemische und physikalische Geologie*, 2, pp. 144–164, 1851.

[20] H. O. Hofman and W. Mostowitsch, *Bull. Am. Inst. Min. Eng.*, Vol. 47, pp. 917–939.

[21] "Sulla formazione terziaria nella zona solfifera di Sicilia," *Mem. Com. Geol.*, Vol. 1, 2, 1871 and 1872; also "Formation solfifere de la Sicile," *Bull. d. soc. d'industr. min.*, (2), 10, 147, 1881.

brackish water lakes were supposed to have been fed by springs bringing the sulphur and calcium carbonate in one of two possible forms, either as H_2S and the bicarbonate of calcium, or else as a monosulphide of calcium. Mottura was likewise of the opinion that the CaS was the result of the reduction of the sulphate by organic matter under the influence of internal heat. Like Mottura, A. von Lasaulx[22] considered fresh-water basins the recipients of thermal springs which contained both H_2S and $CaCO_3$. G. Spezia[23] has developed a similar theory, believing, however, that thermal springs carrying $SrSO_4$, SiO_2, as well as $CaCO_3$ and H_2S in solution deposited their load in shallow sea basins.

According to L. Baldacci[24] the gypsum found associated with the sulphur must be regarded as the result of concentration of marine water in broad, shallow lagoons. This gypsum, which is considered the source of the sulphur, is thought to have been reduced to the sulphide by the action of the hydrocarbon methane, which was discharged in the lagoons by mud volcanoes (maccalube). However, if methane is to act as a reducing agent, it must itself in turn be oxidized. Inasmuch as a temperature of approximately 500° C. is required to induce CH_4 to unite with free oxygen, it would hardly seem probable that this gas could withdraw oxygen from a sulphate at an ordinary temperature. The theory of the reduction of gypsum by hydrocarbons finds another advocate in R. Travaglia.[25] He does not, however, consider the origin of the hydrocarbons the product of maccalube, but rather the result of the decay of concentrated organic matter.

O. Stutzer[26] emphasizes the sedimentary origin of these de-

[22] *Neues Jahrb.*, p. 490, 1879.

[23] "Sull'origine del solfo nei giacimenti solfiferi della Sicilia, Torino," 1892; ref. *Neues Jahrb.*, 1, p. 281, 1893; also *Ztschr. f. Kristallogr.*, Vol. 24, pp. 412–414, 1895.

[24] "Descrizione geologica dell'Isola di Sicilia," *Mem. descritt. d. Carta geol. d'Italia*, 1, pp. 331–374, 1886.

[25] "Contributo agli Studii sulla genesi dei giacimenti di solfo," *Boll. d. R. Com. Geol. d'Italia*, Vol. 20, pp. 110–118, 1889; ref. *Neues Jahr.*, Vol. 2, p. 74, 1892; also F. Fuchs and L. De Launay, "Traité des Gites Minéraux et Metallifères," Vol. 1, p. 273, 1893.

[26] "Die Wichtigsten Lagerstätten der Nicht-erze," Vol. 1, pp. 254–262, 1911; *Zeit. deut. geol. Ges.* (Monatsb.), pp. 8–12, 1911.

posits, additional proof of which he finds in the Gessolungo-Trigona Mine, near Caltanissetta. Here he noted two sulphur beds, the lower three meters in thickness, the upper four meters. The two beds are separated by 70 cm. of sterile shale. The new features observed are a cross bedding of some of the strata, and an unconformity in some places between the lower sulphur and overlying shale (Fig. 6). According to Stutzer the sulphur was due to the oxidation of the H_2S but some difficulty is experienced in finding a suitable explanation of the origin of this gas. Two sources are suggested: first, from organic material by putrefaction, and second, from inorganic sulphates through reduction, attention being called to the fact that the organic material necessary for the reduction is never absent from the sulphur beds. We are led to believe from a statement made on page 259 of his "Lagerstätten der Nicht-erze" that his theory for the Sicilian deposits involves reduction by ascending gases, for he refers in the following words to the reduction of sulphates, the italics are the writer's: "Die bei diesen Prozessen notwendige organische Substanz liefert entweder die gleichzeitig lebende Tier- und Pflanzenwelt oder sie wird in Form von Gasen von unten her zugeführt. *Destillation bituminöser Sedimente, z. B. in Sizilien;* Entgasung von Steinkohlenflozen, z. B. bei Kokoschütz in Oberschlesien."

A theory that would seem in harmony with geological facts should explain not only the presence of the sulphur beds in the limestone and their absence in the gypsum above, but also their formation at normal temperature and under circumstances which will confine the formation and deposition of the sulphur to these land-locked basins or lagoons, the general outlines of which, although badly faulted and eroded, are still nevertheless somewhat retained.

BACTERIAL REDUCTION THEORY.

If we abandon the volcanic idea as the source of the H_2S, we are practically forced to admit that the major portion of this gas must, by some means, be derived from sulphates. It has been shown that the reduction of sulphates by means of CH_4

does not seem probable, and it has also been pointed out that a temperature of approximately 700° C. is necessary for the reduction of calcium sulphate by carbonaceous material. Thus, the inquiry is naturally raised as to whether sulphates are capable of reduction at ordinary temperatures, and if so, what evidence we have of this reaction in nature.

Our attention was first called to the reduction of sulphates at ordinary temperatures, with a resultant liberation of H_2S, by the observations of L. Meyer,[27] F. Cohn,[28] E. Plauchud,[29] A. Etard and L. Oliver.[30] These pioneer investigators failed, however, to distinguish between the microörganisms which possess the power of reducing sulphates with an evolution of H_2S, and the bacteria which thrive in a medium of H_2S, and oxidize this gas to S and H_2SO_4. In the instances referred to, beggiatoa (sulphur bacteria) were believed to cause both reduction and oxidation. It remained for S. Winogradsky[31] to prove conclusively that beggiatoa can perform only the latter function, namely, the oxidation of H_2S to H_2SO_4, and that, in so doing, they accumulate sulphur in their cells as an intermediate product. These organisms are, however, incapable of producing any of the sulphureted hydrogen.

For the first exhaustive study on the sulphate-reducing bacteria, we are indebted to W. M. Beyerinck.[32] In 1895, he was attracted to this problem in an endeavor to explain the abundant liberation of H_2S in the ditches of Amsterdam, especially during the months of July, August and September. As a result of his efforts he was able to isolate one of the anaërobic bacteria capable of causing such a reduction. To it he assigned the name "*Spirillum desulfuricans.*" Beyerinck isolated it in a liter of ditch water to which were added small amounts of mineral salts, sulphates, and traces of organic substances. This addition of or-

[27] *Journ. f. prakt. Chemie*, Vol. 91 p. 5, 1864.

[28] *Ber. botan. Sektion der Schles. Gesellsch. f. Vaterländ. Kultur*, f. 1876, p. 115; ref. *Der Naturforscher.*, Vol. 10, p. 340, 1877.

[29] *Compt. rend.*, Vol. 84, p. 235, 1877; *Compt. rend.*, Vol. 95, p. 1363, 1882.

[30] *Compt. rend.*, Vol. 95, p. 846, 1882.

[31] *Botanische Zeit.*, Vol. 45, Nos. 31–37, 1887.

[32] *Centralbl. f. Bakt.*, 2d Abt., Vol. 1, pp. 1, 49, 104, 1895.

ganic material was essential, since the energy necessary to bring about the reduction of sulphates can be supplied only by the oxidation of this organic material. The reducing powers of his cultures were tested accurately by titrating the H_2S evolved with a standard solution of iodine. Of the numerous experiments described by Beyerinck, in which various sulphates and organic materials were tested, we will refer only to one, which is of especial interest inasmuch as the sulphate reduced was gypsum. Trench water (Grabenwasser) was saturated with gypsum, and to each liter of this solution were added 50 mg. sodium malate (to furnish some organic food stuffs for oxidation), 50 mg. asparagin (to furnish some nitrogen), 100 mg. potassium phosphate, and 1 gm. sodium carbonate. In a few days spirillum desulfuricans caused a noticeable reduction. In less than three weeks the reduction increased to almost 60 mg. H_2S per liter, equivalent to the reduction of 140 mg. SO_3. Beyerinck is convinced that it is immaterial which sulphate is employed. The conditions necessary for an exceedingly flourishing growth of this sulphide ferment are the absence of oxygen, the presence of sulphates, mineral salts, and organic material, and a temperature of about 25–30° C. Some reduction will take place, however, when the temperature is as low as 12° C., or as high as 40° C. The mixed cultures are somewhat more active in producing H_2S than the pure cultures. In nature this organism is found in the slimes, which consist essentially of calcium phosphate and carbonate, with more or less organic material. If iron phosphate is present the slime soon turns black as the result of the formation of a colloidal iron sulphide precipitate.

A. van Delden[33] continued the investigations of Beyerinck, in an endeavor to explain the strong H_2S development in the estuaries (Wadden) bordering the coasts of Holland, where the slime often reaches a thickness of several meters. In order to familiarize himself with the behavior of *Sp. desulfuricans* in fresh water before attempting to isolate the organism responsible for the reduction in sea water, he grew cultures of spirillum desulfuricans and studied the reduction carefully. Some very im-

[33] *Centralbl. f. Bakt.*, 2d Abt., Vol. 11, pp. 81, 113, 1903.

portant facts were here brought to light. In one case, it was found that the trench water contained sufficient organic food material to cause the entire elimination of sulphates from solution. In other instances, when the evolution of H_2S ceased, the addition of more organic material caused the evolution of this gas to be renewed, and the development of sulphureted hydrogen continued as long as sulphates remained in solution. Since unusual interest is attached to the reduction of calcium sulphate, gypsum, we may here cite a few of the experiments using this substance.

Culture Solution.	No. of Days.	Mg. H_2S Liberated per L.	Mg. SO_3 Reduced per L.
Ditch water .....500.00 gms. Potassium hydrogen phosphate 0.250 Sodium lactate..... 2.500 Asparagine ..... 0.500 Gypsum..... 0.150	7	93.5	220
Same as above with gypsum.. 0.300	7	110	260
Same as above with gypsum.. 0.450	7	122	288
Same as above with gypsum.. 0.600	26	187	440

On another occasion, again using gypsum (0.500 gm.), van Delden found that after a period of forty-one days the mixed cultures liberated 246 mg. H_2S per liter, an amount equivalent to that resulting from the reduction of 580 mg. SO_3. Thus it will be seen that large quantities of this gas can be set free without producing injurious effects upon the organisms themselves. Investigations with pure instead of mixed cultures gave quite analogous results, as in one instance the H_2S titrated was equivalent to 238 mg. per liter. It is van Delden's opinion that the organic compounds found in nearly all polluted waters can be utilized by these organisms during the process of reduction. The earlier work of Beyerinck on the reduction of sulphates at room temperatures is fully substantiated by this later investigation.

By employing practically the same culture solutions as were used with *Sp. desulfuricans,* with the addition, however, 3 per cent. sodium chloride, van Delden was able to obtain pure

cultures of the specific organisms active in the reduction of sulphates in sea water. The sulphide ferment active in sea water, although very similar to that of *Sp. desulfuricans,* is nevertheless sufficiently different in its behavior towards sodium chloride solutions to be considered an independent species. To this organism van Delden assigned the name of *Microspira æstuarii.* In the experiments employing mixed cultures of *Microspira æstuarii* the H_2S content evolved totaled in several instances almost four times the maximum noted with *Sp. desulfuricans* in fresh water. Two interesting cases in which mixed cultures were used will be here cited.

Culture Solution.	No. of Days.	Mg. H_2S Liberated per L.	Mg. SO_3 Reduced per L.
Sea water from the Helder ... 500.00 gms. K_2HPO_4 ..... 0.25 Asparagine ..... 0.50 Sodium lactate ..... 2.50 Slime from the Dollard	27	843	1984
Tap water ..... 500.00 NaCl ..... 15.00 K_2HPO_4 ..... 0.25 Asparagine ..... 0.25 Sodium lactate ..... 5.00 $MgSO_4.7H_2O$ 4.00	19	1030	2424

From results of this character, one is amazed at the enormous quantities of H_2S liberated per liter of solution. In the second experiment quoted above, the amount of sulphate reduced exceeds the average sulphate content of sea water. Thus it will be seen that if organic food stuffs are sufficient the sulphates of the ocean can be completely eliminated. If pure instead of mixed cultures were used, similar results were obtained, a maximum of 952 mg. H_2S per liter being recorded, an amount equivalent to that derived from the reduction of 2,240 mg. SO_3.

Van Delden pointed out that *Sp. desulfuricans* and *Microspira æstuarii* are two distinct species and not modifications of the same one, and he found proof of this fact in their behavior towards solutions of NaCl. The following table strikingly illustrates the effect of varying amounts of NaCl upon each.

Per Cent. of NaCl Solution.	0	½	1	1½	2	2½	3	6	8	10
Sp. desulfuricans, mg. SO_3 reduced per L	532	500	528	532	320	80	0	—	—	—
M. æstuarii, mg. SO_3 reduced per L	0	240	1,000	1,200	1,140	1,108	1,280	1,440	600	200

From this table it is apparent that, while both organisms can flourish in brackish waters which contain only a small amount of NaCl (.5 to 1.5 per cent.), when the NaCl content exceeds 2 per cent. the reduction by *Sp. desulfuricans* rapidly diminishes, ceasing entirely at 3 per cent. *M. æstuarii,* on the other hand, continues briskly the evolution of the H_2S in salt concentrations up to 6 per cent. Beyond this point, with further addition of NaCl, the reduction is quickly checked.

That the reduction of sulphates is very general in nature at the present time is evidenced by numerous references in the literature. While only two specific organisms have thus far been thoroughly tested, others will probably be found to possess the same property, in fact, names have been assigned to species which are supposed to perform in a similar manner. As it does not seem necessary to discuss in detail further investigations along this line, brief statements of a few of the most striking instances may be of service in illustrating the universal occurrence of this reduction.

N. Zelinsky[34] examined samples of ooze from the bottom of the Black Sea at depths of 16, 40, 389, 870, and 1207 fathoms and succeeded in isolating an organism capable of reducing sulphates to sulphides under anaërobic conditions. This motile, somewhat elongated bacterium has received the name of *Bacterium hydrosulfureum ponticum.* E. Brusilowsky[35] reported in the estuary of Odessa, a bacterium active in reducing salts of sulphur and oxygen to H_2S. To this organism he assigned the name of *Vibrio hydrosulfureus.* Nadson[36] has pointed out a similar re-

[34] J. Russ, *Chem. Soc.,* Vol. 25, p. 298; ref. *J. Chem. Soc.,* Vol. 66, part 2, p. 200, 1894.

[35] *Russk. Wratsch,* pp. 717, 791, 819, 1890; ref. *Centralbl. f. Bakt.,* Vol. 10, p. 194.

[36] "Ueber die Schwefelwasserstoffgärung in Weissowo-Salzee und ueber die Beteiligung der Mikroorg. in der Bildung des Schwarzen Schlammes," Petrograd, 1903; ref. W. Omelianski, Lafar, "Handbuch der Technischen Mykologie," Bd. 3, p. 214, 1904–1906.

duction of sulphates by *Proteus vulgaris* and *Bac. mycoides* in the black slimes of the "Weissowo-Salzee" (Gouv. Charkow, Russia). N. Goslings,[37] likewise, while unable to obtain pure cultures of the organisms, was convinced that microörganisms were the cause of the H_2S noted in the Passuger Ulricus water, a strongly alkaline and iron-bearing spring rich in sulphates. A microörganism quite similar to Beyerinck's *Sp. desulfuricans,* if not identical with it, was isolated by Anton Rank.[38]

In determining the cause of the excessive production of hydrogen sulphide in three sewage disposal plants, W. M. Barr and R. E. Buchanan[39] decided that the organic matter in normal sewage does not contain enough sulphur to produce the quantities of H_2S observed. Chemical analyses of the raw sewage and effluents were made and it was found that where the sulphates in the original water supply are high, there is a marked reduction in the amount of mineral sulphates found in the effluent, showing that a portion of these mineral sulphates had been reduced and removed from solution.

Another instance suggestive of reducing organisms came under the observation of the United States Geological Survey.[40] A quantity of water rich in sulphates, from one of the alkaline lakes of California was sent to the laboratory in a wooden barrel. When received, the water had become so saturated with H_2S and discolored by extract from the wood, as to be rendered unfit for analysis.

In the open sea, however, due to oceanic currents and the presence of large amounts of ferruginous clays, little opportunity is offered for the accumulation of the H_2S, formed by either reducing bacteria or the bacteria of decay. The sulphureted hydrogen evolved would be quickly dissipated in the vast expanse of water, or else would find combination with ferruginous compounds. While the low temperature of the oceanic depths no doubt retards the reduction, this process does, nevertheless,

[37] *Centralbl. f. Bakt.,* 2 Abt., Vol. 13, p. 385, 1904.

[38] "Beiträge zur Kenntnis der Sulfatreduzierenden Bakterien," Diss. phil. Zürich, 1907; ref. *Centralbl. f. Bakt.,* 2 Abt., Vol. 20, p. 6119, 1907–1908.

[39] *J. Ind. and Eng. Chem.,* Vol. 4, p. 564, 1912.

[40] F. W. Clarke, U. S. Geol.. Survey, Bull. 491, p. 101, 1911.

take place, especially in the waters of the sea bottom that are in contact with the "blue muds." J. Murray and R. Irvine[41] observed that in the water filtered from the "blue muds" the sulphur content was reduced from 25 to 50 per cent. of that originally present in the sea water. The soluble sulphates of the alkalies and alkaline earths in the waters of the sea bottom are thus removed from solution and largely replaced by carbonates and insoluble sulphide. It is this precipitate of iron sulphide which is the cause of the blue black color of the "blue muds."

Entirely different conditions are encountered when the same reactions take place in lagoons, or land locked basins, where oceanic currents are absent and when the iron salts are insufficient to combine with all the H_2S liberated. We are now approaching the conditions which we might very reasonably believe to have existed in the lagoons of the sulphur districts of Sicily. To prove that large accumulations of H_2S can result in lakes or land lock basins, one need only to observe what is taking place at present in the Weissowo-Salzsee (Gouv. Charkow, Russia) or the Black Sea.

In the ground water of the Weissowo-Salzsee we have a remarkable instance of H_2S concentration with depth. Nadson, who isolated reducing bacteria in the slimes of this lake, has reported the following amounts of sulphureted hydrogen in one liter of the water:

At a depth of 16 meters	5.91 c.c. H_2S.
At a depth of 18.1 meters	88.31 c.c. H_2S.
At a depth of 18.7 meters	184.96 c.c. H_2S.

These same biochemical forces are also operative at the present time in the Black Sea. In the latter case, however, due to the enormous volume of water involved, and the large influx from the Mediterranean by way of the Bosphorus, the quantity of H_2S per liter is not as large as in the preceding instance. Nevertheless, the Russian deep sea expedition of 1891 detected sulphureted hydrogen everywhere beginning at depths of about 200

[41] *Trans. Roy. Soc. Edinburgh*, Vol. 37, p. 481, 1895; also Challenger Rept., "Deep-sea Deposits," p. 254, 1891; W. N. Hartley, *Proc. Roy. Soc. Edinburgh*, Vol. 21, p. 25, 1897; Murray and Irvine, *idem*, p. 35.

meters. Below this level the amount of H_2S increased quite rapidly as was shown by A. Lebedinzeff.[42] The amount of this gas in 100 liters of water varied with the depth as follows:

At a depth of 213 meters	33 c.c. H_2S.
At a depth of 427 meters	222 c.c. H_2S.
At a depth of 2,026 meters	555 c.c. H_2S.
At a depth of 2,528 meters	655 c.c. H_2S.

From this table it will be seen that the bottom layers contain over twenty times as much H_2S as those nearer the surface. According to N. Zelinsky and E. Brusilowsky this development of gas is due to the action of anaërobic bacteria upon the sulphates in solution. Below the 200-meter level, all the higher forms of life disappear, as a result of the poisonous action of this gas and the absence of free oxygen in the water. As a consequence, only about 7 per cent. of the maximum depth of the Black Sea is habitable. N. Androussow[43] is inclined to believe that a portion of the H_2S is derived from decaying organic material. The poverty of the bottom layers in free oxygen and the stagnant condition of the water below the 200-meter level, is due to the prevention of normal vertical circulation, resulting from the increase of specific gravity with depth.

If the present be considered a "key to the past," the biochemical reactions which one may observe taking place to-day in the Black Sea are quite suggestive of what we might reasonably expect to have occurred in an earlier geological period in the lagoons of the sulphur districts of Sicily. There is, however, this difference to be noted between the Black Sea of the present time and land-locked basins of Sicily of late Miocene. In the former, we have an unusually large enclosed body of water reaching in places a depth of over 2,500 meters, and possessing an average annual temperature of about 10° C. In spite of the enormous volume of water and the comparatively low temperature, suffi-

[42] *Travaux de la Soc. des naturalistes à Odessa*, 1891, Vol. 16; ref. W. Omelianski Lafar, "Handbuch der Technischen Mykologie," Bd. 3, p. 214.

[43] *Bullétin de la Soc. Impêr. de Géographie*, 1892, Vol. 28, p. 370; *Mémoires de l'Ac. Imp. Des Sciences de Petrograd*, 1894; Vol. 1, p. 1; "Guide des excursions du VII. Congl. géol. internat.," No. 29, 1897.

cient H_2S has been developed to destroy all the higher forms of life below the 200-meter level. In Sicily, on the other hand, the lagoons or bays, while connected with the sea by shallow channels, were otherwise cut off from oceanic circulation by a bar. These lagoons were much smaller in extent, probably not over 12 km. in length and 2 km. in width, while the average temperature of the water, due to its geographical location, must have been considerably higher than that of the Russian lakes of the present time. An extremely energetic liberation of H_2S would be the direct result of reduction in the warm waters rich in sulphates, as the experiments with *Sp. desulfuricans* and *M. æstuarii* have demonstrated a maximum liberation of gas when the sulphates were abundant and the temperature in the vicinity of 20–25° C. Inasmuch as the bodies of water were small and the reduction probably continued for several thousand years, not only would the lower levels of the basins become practically saturated with sulphureted hydrogen, but other important chemical reactions would result.

An attempt will here be made to trace the various chemical changes which very likley took place in the lagoons while the waters were being concentrated by solar evaporation and the soluble sulphates reduced by anaërobic bacteria. Originally, the basins probably swarmed with marine life, and, by the death and resultant decay of these organisms, some H_2S was unquestionably developed. In the process which we term putrefaction, the proteid material is acted upon by numerous bacteria, and, after passing through a series of intermediate stages, finally liberates H_2S. The nitrogenous material which is also present in animal tissue would likewise break down, yielding ultimately NH_3, which combining with the CO_2, would form $(NH_4)_2CO_3$. This salt is everywhere present in the ocean, owing to the decomposition of albuminoid material. This alkali would possess the property of converting some of the sulphate and chloride of calcium, present in sea water, to the carbonate. The equations for these reactions may be expressed as follows:[44]

[44] "Report on the Deep Sea Deposits," Challenger Expedition, 1891, p. 254.

(1) $CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4$,
(2) $CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$.

Thus, while some of the H_2S, especially in the early stages of the concentration, was undoubtedly derived from processes involving putrefaction, the comparatively few fossils found in the sulphur-limestone series, would preclude the possibility of the formation of all of this gas in that manner. The major portion of the sulphureted hydrogen must have been derived from another source, namely from the reduction of sulphates in solution through the action of anaërobic bacteria. The sulphates present in quantity in sea water are the sulphates of calcium, magnesium and potassium, and these salts must be considered the raw material for the development of the greater portion of the H_2S.

We are not familiar with the exact manner in which these organisms bring about reduction, but we have ample proof of the disappearance of the sulphates in solution, and of the generation of H_2S in quantity. If we assume, as seems plausible, an intermediate product, namely, a sulphide, and follow the suggestion of Murray and Irvine that the reduction is produced by the carbonaceous material of the protoplasm, the equation in the case of calcium sulphate would be expressed as follows:

(3) $CaSO_4 + 2C$ (living microörganisms) $= CaS + 2CO_2$.

The CaS formed as an intermediate product, though only slightly soluble in water, is nevertheless hydrolyzed by it and yields soluble products.[45]

(4) $CaS + 2H_2O = Ca(OH)_2 + Ca(SH)_2$.

In all the investigations involving the reduction of sulphates by microörganisms the presence of some organic material is essential, as the energy necessary to bring about the reduction can only be secured by the oxidation of this organic matter. The dark-colored bituminous rocks of the sulphur horizon are sufficient proof of the existence of an adequate amount of this important

[45] R. Abegg's "Handbuch der anorganischen Chemie," Vol. 2, part 2, p. 117, 1905.

prerequisite. The CO_2 liberated by such oxidation would react upon the products of equation (4), forming compounds as expressed in equation (5).

(5) $Ca(OH)_2 + Ca(SH)_2 + 2CO_2 = 2CaCO_3 + 2H_2S.$

Hydrogen sulphide would thus be generated in the lower levels of the enclosed basin, and, at the same time, a precipitate of $CaCO_3$ would result.

The sulphate of potassium, which is also present in the sea water, would likewise be reduced and follow the reactions indicated above for the calcium salt. The K_2CO_3, however, by virtue of its solubility would not separate from solution. In like manner the magnesium sulphate would suffer reduction, but the $MgCO_3$ ultimately formed would be held in solution by the ammonium salts, especially the chloride, formed as illustrated in equation (2). Thus while the sulphates of calcium, magnesium and potassium are all subject to reduction, only the calcium carbonate would precipitate in quantity. The actual occurrence of the sulphur in a limestone is in harmony with this deduction. The H_2S liberated would soon poison the lower layers and drive the fauna to the upper levels. With the continued evolution of this gas and its diffusion upward, practically the entire land locked area would, in a short time, geologically speaking, be rendered unfit for marine habitation. It should be borne in mind that in the early stages of concentration, the H_2S was probably the result of the combined action of putrefaction and reduction. With the continued liberation of H_2S, the fauna would be removed from the depths and restricted to the surface levels. Their number being thereby largely reduced, the H_2S resulting from the putrefaction of a limited number would likewise be materially diminished. On the other hand, the evolution of H_2S as a result of the reduction of sulphates would become relatively more important with the disappearance of the fauna from the lagoons.

The H_2S in diffusing upward would, upon reaching the surface, be oxidized to water and sulphur.

(6) $H_2S + O = H_2O + S.$

This reaction can proceed as a purely chemical process although it is not at all improbable that the sulphur bacteria may have aided somewhat in the separation of free sulphur.

Part of the sulphur thus set free by the oxidation of the H_2S would slowly settle to the bottom of the basin and become disseminated throughout the limestone. Aside from occurring disseminated, the sulphur is also found in small horizontal bands or seams varying in thickness from 5 mm. to 2 cm. This observation would lead one to infer that at certain intervals a more copious precipitation of sulphur had taken place, and our next thought will be directed to a solution of this phase of the problem.

E. Divers and T. Shimidzu[46] have shown that calcium hydrosulphide reacts very readily with sulphur to form a calcium polysulphide, while at the same time H_2S is liberated. This observation, as will be seen, has a direct bearing upon the chemical reactions concerned in an explanation of the horizontal bands of pure sulphur. Some of the finely divided sulphur resulting from the oxidation of the H_2S would not reach the bottom of the enclosed basin, but would react with the $Ca(SH)_2$ which had been formed according to equation (4). This experiment was repeated by the writer, who used liter flasks, flowers of sulphur, calcium monosulphide and water in an endeavor to determine whether a polysulphide would be formed at room temperature. The dark amber color and increased specific gravity of the resulting solution, gave unmistakable evidence of a solution of some of the sulphur in the hydrosulphide, and of the formation of a polysulphide at a temperature which did not exceed 25° C. If the calcium hydrosulphide dissolves some of the finely powdered flowers of sulphur at room temperatures, freshly precipitated sulphur would react much more energetically. The experiments of R. H. Brownlee[47] and H. C. Cooke[48] have shown that freshly precipitated sulphur is considerably more active chemically than other forms of the same element. The calcium

[46] *Jour. Chem. Soc.*, Vol. 45, p. 283, 1884.
[47] *Jour. Am. Chem. Soc.*, Vol. 29, p. 1032, 1907.
[48] *Jour. Geol.*, Vol. 21, p. 25, 1913.

tetra or penta sulphide would probably be the result of the action of the freshly precipitated sulphur and calcium hydrosulphide, and the equation could be expressed as follows:[49]

$$(7) \qquad Ca(HS)_2 + 4S \rightleftarrows CaS_5 + H_2S.$$

Divers and Shimidzu have pointed out that the reaction (7) between calcium hydrosulphide and sulphur is reversible, that is, the polysulphide of calcium is very unstable, and H_2S coming in contact with such a solution, would produce an exceedingly heavy precipitate of free sulphur. "The calcium becomes hydrosulphide, and if the solution is cold and sufficiently dilute, all polysulphide is destroyed as is seen from the bleaching of the solution." The polysulphide obtained by the writer by dissolving flowers of sulphur in an aqueous solution of calcium sulphide at ordinary room temperature, responded in the same manner when H_2S was passed through the solution. We now have what seems to be a satisfactory explanation of the banded structure observed in much of the Sicilian limestone. The formation of a polysulphide, followed by its immediate decomposition, would produce at intervals larger quantities of free sulphur, which would form the horizontal seams or bands in the calcium carbonate rock.

The maccalube or mud springs, which we may still see in operation in the vicinity of Girgenti and Caltanissetta, were probably more active in earlier geological periods. The intermittent discharge from these mud springs was probably the result of a derangement of the ground waters due to seismic disturbances. Salty, bituminous clays were thus brought from the lower horizons and deposited in the lagoons while the precipitation of sulphur was in progress. This material, which forms the sterile intercalations between the sulphur beds, has been given the name of tufi.

While the reduction of sulphates was taking place in these

[49] H. V. Tartar, *Jour. Am. Chem. Soc.*, Vol. 36, 495, 1914, has shown that calcium tetrasulphide is the lowest polysulphide formed when $Ca(OH)_2$ and S react in aqueous solution. When sulphur is in excess it combines with the tetrasulphide to form the pentasulphide.

land locked basins, evaporation of the enclosed water was likewise in progress. According to J. Usiglio,[50] when concentration of sea water equivalent to about one fifth of the original volume results, the saturation point of gypsum is reached and this mineral begins to separate out. That the saturation point of gypsum had been reached in the sulphur districts is clearly shown by the massive deposits of this mineral usually found above the sulphur-limestone series. At Comitini the concentration had even proceeded far beyond this point, for here rock salt has been found above the sulphur bed. With this concentration, due to solar evaporation, an additional factor is introduced which ultimately checks further reduction. The amount of solid matter present in solution in the oceanic waters varies considerably with location. Analyses of waters from the eastern Mediterranean,[51] collected during the voyages of the Austrian steamer "Pola," showed a salinity varying from 3.836 to 4.115. Of all the salts present in solution, sodium chloride is by far the most abundant single constituent, W. Dittmer's[52] estimate being 77.758 per cent. If we consider the salinity of the lagoons at the beginning of the concentration period at approximately 4 per cent., and if three fourths of all the soluble salts was sodium chloride, there would have been present at the outset about 3 per cent. NaCl in the water subjected to bacterial reduction. By the time the concentration had reached the stage at which gypsum began to precipitate—a concentration equivalent to about one fifth of the original volume—the salinity of the water in the lower levels of the basins must have increased about five fold. Likewise the sodium chloride content, at the time of the separation of the gypsum, must have experienced a like increase. We know that NaCl, in general, has an inhibitory action on bacterial growth,[53] especially when present in amounts exceeding 6 to 8 per cent. A. van Delden[54] has studied the effect of NaCl upon *M. æstuarii,* one of

[50] *Ann. chim. phys.,* (3), Vol. 27, pp. 92, 172, 1849.

[51] Analyst, K. Natterer, *Monatsh. Chemie,* Vol. 13, 1892, pp. 873, 897; Vol. 14, 1893, p, 624; Vol. 15, 1894, p. 530.

[52] Challenger Rept., "Physics and Chemistry," Vol. 1, p. 203, 1884.

[53] K. v. Karaffa-Koroutt, *Z. Hyg.,* Vol. 71, p. 162.

[54] *Centralbl. f. Bakt.,* 2 Abt., Vol. 11, p. 116, 1903.

the most active of the sulphate reducing organisms. From the table given on page 566, it will be seen that reduction was quickly checked when the sodium cholride content exceeded 6 per cent. Thus, by the time the gypsum began to separate from solution, the increased NaCl content had reached such proportions as to check completely further bacterial action. If this be correct, we have an explanation for the absence of true sulphur-limestone beds in the gypsum above. Occasionally sulphur is found in the gypsum, but only in very small, irregular, lens shaped masses of pure sulphur which probably represents secondary accumulations. Mottura has called attention to the solvent action of oils emanating from the asphaltic material which permeates the limestone-sulphur zone. Likewise the natural etch figures seen on many of the sulphur crystals are further evidence that a solvent has been active in the transportation and formation of the secondary sulphur.

If, after the concentration had proceeded to the point of deposition of the gypsum, a subsidence of the land should take place or a severe storm destroy the bar which separates the water of the lagoon from oceanic circulation, the influx of water from the ocean would materially decrease the salinity and NaCl content to such a point that reduction might be renewed. We should then have developed a limestone-sulphur zone near the top as well as near the bottom of the gypsum formation, as is the case near San Cataldo, Fig. 4.

At the close of the Miocene, a gradual subsidence of the land took place, again establishing communication with the open sea. The subsidence continued until a noteworthy depth had been reached for in the sea foraminifera were abundant. This fact is revealed by the presence of a white foraminiferous limestone resting conformably upon the gypsum-sulphur-limestone series.

SUMMARY.

The sulphur deposits of Sicily constitute isolated, basin-like formations scattered throughout the south-central portion of the Island. The sulphur bearing stratum is usually underlain by

tripoli, while massive deposits of gypsum rest conformably upon it. That portion of the sulphur which is occasionally found in small, irregular lens-shaped masses enclosed in the gypsum, seems to represent secondary accumulations. These are so limited in extent as to be of economic importance only when found in the proximity of the true sulphur beds. The sulphur beds vary greatly in thickness, the average approaching probably three or four meters. Generally, in any given locality, three or four beds are encountered, one above the other, separated by narrow, sterile layers of bituminous, salty shales. These sterile intercalations rarely exceed three feet in thickness, and probably represent intermittent discharges from "maccalube" into the basins during the deposition of the sulphur. In the sulphur beds the sulphur occurs not only disseminated throughout a limestone, which is more or less bituminous in character, but also in bands of almost pure sulphur, from 5 mm. to 2 cm. in thickness, which extend parallel to the bedding.

The earlier theories proposed laid unusual stress upon the direct influence of volcanism with a resultant deposit formed under strictly igneous conditions. As the sedimentary character of the beds was unquestionably established, the idea of the influence of volcanism was partially relinquished, at least to such an extent as to permit a deposition under aqueous conditions.

While it has been universally accepted that the sulphur was the result of the oxidation of H_2S, the source of the sulphureted hydrogen has given rise to much speculation. Theories involving the reduction of gypsum by methane or by organic matter seem to have at present the largest number of adherents. It does not seem possible that either methane or lifeless carbonaceous material could possibly have reduced the gypsum at ordinary temperatures and there are no features present which would indicate unusual thermal conditions.

Numerous observations in nature of copious liberation of H_2S in both fresh and saline waters rich in sulphates, have led to the belief that living microörganisms are able to cause a reduction of sulphates in solution at ordinary temperatures. This belief

has been repeatedly verified in the laboratory by bacteriologists, who have isolated specific anaërobic bacteria capable of performing this function. The accumulation of H_2S set free by sulphate reducing bacteria has rendered the lower levels of some of the present lakes and enclosed basins uninhabitable for the higher forms of life. In the Black Sea, at the present time, only seven per cent. of the maximum depth is habitable as the result of the poisonous action of this gas.

These observations are unquestionably suggestive of what we may reasonably expect to have taken place in an earlier geological period in the lagoons of the sulphur districts of Sicily. The small size of the individual basins, the comparatively high average temperature of the water, due to its geographical location, the high sulphate content, and the period of years over which these bacterial reactions extended, probably caused a liberation of H_2S sufficient not only to saturate the lower levels, but also to bring about important accompanying chemical reactions. The oxidation of H_2S and the action of CO_2 upon $Ca(OH)_2$ and $Ca(SH)_2$, products formed by the reduction of calcium sulphate, would cause a simultaneous separation of the sulphur and a precipitation of calcium carbonate. Some of the sulphur would, however, be absorbed by the $Ca(SH)_2$ to form a polysulphide. This polysulphide is so unstable that even H_2S coming in contact with such a solution would produce a heavy precipitate of free sulphur. The formation of a polysulphide, followed by its immediate decomposition, would liberate at intervals sufficient sulphur to form the horizontal bands in the limestone. While the reduction was in progress, evaporation was likewise taking place. Thus, by the time the concentration had reached the saturation point of gypsum, the increased sodium chloride content of the basin had reached such proportions as to completely check further bacterial action. A destruction of the bar which separated the lagoon water from oceanic circulation, or a gentle subsidence of the land, might cause such an influx of water from the ocean as to decrease to a marked extent the salinity of the water. Reduction would then be once more renewed, after con-

siderable gypsum had been deposited. Ordinarily, however, the sulphur-limestone series is confined to the base of the gypsum formation.

Such a bacterial reduction theory, with its accompanying chemical reactions, would explain the presence of disseminated and banded sulphur in the limestone, the usual absence of the sulphur-limestone rock in the gypsum above, and the formation of the sulphur at normal temperatures and under conditions which would confine its formation and deposition to these land-locked basins.

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DISCUSSION

This department has been established by the editors in order to afford to those interested in questions relating to economic geology an opportunity for informal discussion. Contributions are cordially invited either in the form of discussion of more formal papers appearing in earlier numbers or bearing upon matters not previously treated. Letters should be directed to the Editor, Sheffield Scientific School of Yale University, New Haven, Conn. The full name of the author should be attached to all communications.

PRECIPITANTS OF GOLD AND SILVER.

Sir:—In an article on "Metallic Minerals as Precipitants of Gold and Silver" (ECON. GEOL., March, 1914), Messrs. Palmer and Bastin state that metallic silver is precipitated from a solution of silver sulphate by the mineral covellite.

As it seemed impossible to account for such a reaction either by equation or theory, the work of Palmer and Bastin on covellite was repeated with the following results:

A piece of covellite was carefully cleaned, freed from coatings of pyrite and weighed. This was then immersed in 50 cc. of an N/40 solution of silver sulphate.

As Palmer and Bastin noted, a crystalline deposit formed within a few minutes and these crystals increased in number with time, some of them remaining on the covellite and others dropping to the bottom of the tube.

The solution was tested from time to time and it was found that all of the silver was removed from solution at the end of a week. The solution in the tube had in the meantime become quite blue due to dissolved copper.

The crystals which had formed were collected on a Gooch filter, washed, dried and weighed. They were then treated with dilute nitric acid which will dissolve metallic silver. The crystals, however, were not attacked even on warming. The addi-

tion of more nitric acid effected their solution, but a small dark-colored residue remained.

The solution was filtered and the silver precipitated as silver chloride, filtered, washed, dried and weighed.

From .0358 gram of crystals, .0279 gram of silver chloride was obtained which is equivalent to .0209 gram of silver. The amount of silver in the original solution was 0.1143 gram. The amount not found in the crystals was found on the surface and in the interstices of the covellite. These figures indicate that the crystals were not metallic silver but some compound of silver.

The question now must be answered as to what the composition of the crystals really is.

Of the possible combinations there might be: Ag_2S; AgCu; $x(CuS)\cdot y(Ag)$; or $x(CuS)\cdot y(Ag_2S)$. If we calculate what weights we might have of these compounds, using the weight of silver found in the analyzed crystals, we find that we should have .0240 gram Ag_2S, which leaves .0118 gram of crystals unaccounted for. Calculated to AgCu, we have .0332 gram which gives a difference of .0026 gram. This is not great, but this type of compound is not at all probable, if indeed possible.

Some of the crystals precipitated from the silver sulphate solution were submitted to Professor A. C. Gill for examination. He states that while these crystals appear to have very nearly the color of silver, the habitus is such as to indicate that they do not belong to the regular system. An orthorhombic or monoclinic symmetry seems most probable, from such examination as could readily be made. They do not appear to be silver. This examination seems to indicate that the crystals are not mixtures of CuS and silver.

If the silver found be calculated to a mixture of copper and silver sulphides such as $(AgCu)_2S$, the weight would be .0363 gram which differs from the actual weight of crystals by .0005 gram. $(AgCu)_2S$ is the mineral jalpaite or stromeyerite.

Another set of determinations was made to check these results and it was found that .0450 gram of crystals contained .0386 gram of silver, which shows conclusively that the crystals are not metallic silver.

If this amount of silver is calculated to $(AgCu)_2S$, the weight is .0670 gram, but if calculated to Ag_2S, the weight is .0443 gram. In this case, evidently, the Ag_2S formed has not combined with CuS to form $(AgCu)_2S$ and so the conclusion must be drawn from these combined experiments that in silver sulphate solutions covellite will take silver out of solution forming Ag_2S which combines with various proportions of CuS.

H. W. ELLEY.

ITHACA, N. Y.

OIL IN AN IGNEOUS ROCK.[1]

Sir: The writer recently had occasion to communicate to the *Oil and Gas Journal* (April 22, 1915) some observations, on a unique occurrence of oil in a new field near Thrall in Williamson County, Texas. This field furnishes a new illustration of the variety of geological conditions which have led to the accumulation of liquid hydrocarbons, and it seems worth the while to relate the facts now known, to the scientific public.

The rock reservoir holding the oil in the Thrall field is believed to be a submarine eruptive, now largely changed to serpentine. It is a soft, porous, green rock, originally in part glassy and in part crystalline. Most of the rock contains spherulites and some appears to be amygdaloidal or pumiceous lava. In fact, phenocysts and spherulites may be found in the same thin section. Other parts of the rock seem to be pyroclastic, consisting of angular grains fairly uniform in size. Some is a volcanic breccia.

The rock is undoubtedly related historically and structurally to a series of intrusives and probably submarine extrusives occurring in a belt which parallels the Balcones escarpment. This escarpment is marked by faults and monoclines, and extends from near Rockwall, past Waco and Austin, to San Antonio, and from the latter point westward to the vicinity of Del Rio. East and south of this line the land has sunk to form the Gulf Coastal Plains, while to the north and west lies the Edwards plateau, where the Comanchean rises from 500 to 2,000 feet higher than the Upper

[1] Published by permission of the director of the Bureau of Economic Geology and Technology, University of Texas, Austin, Texas.

Cretaceous in the Gulf Coast Plains. The belt of volcanics follows this line peripherally. It is not a continuous belt, though it is hardly probable that all localities of exposed igneous rocks in the belt are yet known. Some previously unknown localities have been found quite recently within the area of the Austin folio, so well mapped and described by R. T. Hill. A dozen or more outcrops are known in the vicinity of Austin. At Knippa, on the Southern Pacific, and from there to Uvalde and beyond, like intrusives appear in many places. The westernmost occurrences consist of sills capping Turkey, Moros and Pinto Mountains in Kinney County. Some of the volcanics near Austin were regarded by Hill as having been formed by submarine eruptions in the Cretaceous seas, and other geologists hold the same view.

These volcanics are nearly all highly basic, dark, almost black, and heavy. The black rock in Pilot Knob was called nepheline basalt, or limburgite, by J. F. Kemp. It seems to be associated with some pyroclastic layers in the containing terraces. In one of the small outcrops of intrusives in South Austin, the rock is a black basalt, and some of it is also clearly amygdaloidal. A significant feature of all these volcanics is that as a rule they occur in approximately the same stratigraphic horizon. They invade mostly the upper part of the Austin chalk and the lower part of the overlying marl ("Ponderosa marl," Taylor marl).

This is also the position of the oil-bearing serpentine in the Thrall field. It lies at a depth of 820 feet, and the Austin chalk is known to lie, not far distant from the field, at 1,050 feet. Both of these formations are rich in organic remains, especially in foraminifera. Bituminous distillation products can usually be obtained by submitting rock from either formation to sufficiently high temperatures.

The oil is of about the same quality as the best oil from the Corsicana field. It has a gravity of about 0.827. It is red in color. In all probability the oil has slowly filtered into the amygdaloidal, brecciated, porous and in part tuff-like igneous rock body, long after it was buried, in the same manner as it would filter into any other porous rock from contiguous oily marls. There is no doubt that the impure serpentine rock is the porous retainer in

which the oil is now held. The "cap rock" seems to be a very slightly indurated stratum of the Taylor marl, only a few feet in thickness. This is also found to contain oil in some wells. In most wells oil is obtained as soon as the drill enters the underlying green, porous, soft igneous lense. Initial production, so far, has varied in different wells from 20 to perhaps 2,000 bbls. per day, and it has increased with depth of penetration of the oil-bearing rock. This rock is reported to have had a thickness of more than 280 feet in one well; in another case it was 97 feet thick. The first wells were drilled only some twenty feet into the igneous rock. Later, they were deepened and a greater production thus secured. Some drillers claim that all the oil-bearing rock is alike and in one solid sheet. Other drillers claim that there are distinct layers, each several feet thick, differing in hardness and in appearance of the cuttings.

The inexpensive drilling in this field has attracted many operators, and after four months' development, oil tests have already been made in all directions, several miles away from the producing wells. There are now more than sixty producing wells, all located less than a mile apart. The best information, from tests already made, shows that at a distance of about a mile in three directions from the center of the field both the igneous rock and the oil are absent. Too few data are at hand to justify conjectures as to the form or size of the oil-bearing rock or its structural relations, but there can be no doubt that the igneous bodies have formed a structure in the containing marls which retains the oil pool. Four facts seem to be established: (1) The oil occurs in a green, porous, impure serpentine rock, containing augite, olivine, chlorite, epidote and magnetite, which rock originally was a partially glassy, brecciated and amygdaloidal lava; some of the rock, also, being volcanic tuff; (2) this body of altered igneous rock occurs in the Taylor marls not very far above its contact with the Austin Chalk; (3) the igneous body is one of a series of similar bodies recognized from outcrops at the same horizon in a belt outside of the Balcones escarpment; (4) the oil is practically of the same quality as the Corsicana oil, which comes from about the same stratigraphic horizon.

The pores of the rock are in part filled with calcite, apparently introduced with the profound metamorphic change to which the rock has been subjected. A chemical analysis of a sample of this rock from Witherspoon and Fuchs well number 1 has been made by Mr. J. E. Stullken and is as below:

	Per Cent.
Silica	31.55
Alumina	19.69
Oxide of iron	12.44
Lime	5.96
Magnesia	11.08
Sulphuric acid	2.77
Potassium oxide	0.08
Sodium oxide	0.04
Loss on ignition	15.64
	99.25

A petrographic study of the rock is now being made and it is expected that this will throw more light on the real nature of the rock and the conditions under which it was made and later altered.

J. A. UDDEN.

REVIEWS

Sales Potasicas en Cataluña. By CÉSAR RUBIO and AUGUSTÍN MARÍN. Bol. del Inst. Geol. de España, vol. 14, 2d ser., pp. 173–230, 1914.

This report on the recently discovered deposits of potassium salts in the province of Catalonia, Spain, prepared by two members of the staff of the official Geological Survey of Spain, appears to be the first authoritative account of the geology of the deposits. Although the report is of a reconnaissance nature, intended to serve as a basis for future more detailed investigations, it contains much of interest.

The discovery of the potassium salts was due to accident. During the exploration consequent upon the opening up of a salt deposit at Cardona that had been formerly worked, the potassium-bearing horizon was penetrated. So long ago as 1897, however, a Spanish scientist, who was familiar with the deposits of Stassfurt, had called the attention of the government to the advisability of conducting investigations in Catalonia in search of potash deposits, but, as often happens, the advice went unheeded and the recognition of the prophet was deferred until long after the prophecy.

The basin in which the salts occur consists of marine sediments of Eocene and Oligocene age. The stratigraphic sequence in ascending order is believed to be as follows:

1. Marine marls of Eocene age.
2. Bluish gray marls at Suria and Cardona, at which two places they cover the saline deposits.
3. Red gypsiferous marls and gypsum.
4. Sandstones, conglomerates, marls, and red shales; they are considered as the base of the Oligocene.
5. Limestones and fossiliferous marls.
6. Lignitiferous reddish marls.
7. Limestone.
8. Reddish and grayish marls; possibly of middle Oligocene age.

These rocks have been folded into a number of anticlines and synclines. Four anticlinal axes, which are important structural features in connection with the secondary localization of the potassium salts, are shown on the geologic map accompanying the report.

The most important developments have been undertaken near the

town of Suria. The strata here have been folded into an asymmetric anticline, the south limb of which stands almost vertical. About 800 meters south of the axis of this anticline the strata have been faulted, the throw being not less than 100 meters. The saliferous horizon has been explored by borings and by a shaft. The main piece of development work consists of a shaft 68 meters deep. From near the bottom of the shaft a crosscut has been driven and from the face of this a horizontal boring 26 meters long has been made. From the bottom of the shaft a vertical boring was put down, approximately 124 meters deep. The shaft penetrates the reddish marls that cap the saliferous horizon. In the vertical bore hole a saline deposit consisting of an alternation of layers of common salt and carnallite ($KMgCl_3 - 6H_2O$) to the number of thirty layers were cut. A similar succession was also intersected in the crosscut and horizontal boring. The average thickness cut in the two bore holes, figured in equivalents of pure carnallite and sylvinite (the double chloride of sodium and potassium) aggregates 17 meters carnallite and 3.75 to 4 meters of sylvinite. The authors point out, however, that the different bands of carnallite are highly irregular and are not susceptible of accurate measurement. In places the salts form layers, but in other places they cement blocks and nodules of rock salt and fill fissures in the salt, thus giving evidence of transposition and secondary deposition. The rock salt occurs in distinct beds separated by thin laminæ of anhydrite—the typical year rings of the German geologists. The absence of the multiple sulphates of potassium, calcium and magnesium, such as kieserite, polyhalite and others, is noteworthy.

The tonnage of potassium salts indicated is computed to be as follows, the provisional character of the estimates being fully recognized by the authors: carnallite 2,550,000 tons; sylvinite, 1,125,000 tons, a total of 3,675,000. The carnallite of Suria is of a pronouncedly red color. It ranges from 11.52 to 15.26 per cent. of K_2O.

The genesis of the deposits is discussed in some detail. Especial attention is given to those changes that may be expected to occur when a primary potassium-bearing saline is subjected to leaching and redeposition. The arguments are supported by experimental data drawn from the classic investigation of Van t'Hoff on the oceanic salts. They point out that if a deposit of carnalite and sylvinite is subjected to leaching (1) water will dissolve the carnallite in preference to the sylvinite; (2) the dissolved carnallite on reaching a place where the solution becomes concentrated by evaporation or other means, will first deposit sylvite (KCl); and the solutions thus becoming richer in magnesium will permit a renewed deposition of carnallite; and (3) in this way the separation apparently existing between the zones of sylvinite and of carnallite is explicable. It is concluded that the richer deposits of potash occur

near the summits of the anticlines, which are therefore the most promising places to begin prospecting; and that the unaltered deposits occur in the synclines, that they are poorer in grade, and probably lie so deep as not to admit of profitable exploitation. The great value of careful stratigraphic studies in locting the sites for bore holes during prospecting is strongly emphasized.

The discovery is regarded in the present stage of development as of the nature of a local or private resource, but it is confidently believed that a systematic campaign of prospecting will surely elevate it to the rank of a national resource. It is estimated that the deposits will be able to supply the local market at prices very much less than those imposed by the German Kali Syndicate and will therefore tend to augment the use of potassium salts in Spanish agriculture, in which respect Spain lags far behind other nations. On account of these various considerations it is advised that the state should not hesitate in the work of investigation of the deposits, inasmuch as the results that will accrue to the nation will be of incalculable value.

The nearest analogues of the Spanish deposits are those of upper Alsace, which have been under exploration by means of borings during the last ten years. By these explorations a basin of lower Oligocene age has been outlined, which is estimated to contain 300,000,000 tons of pure K_2O—sufficient, at the present rate of consumption, to supply the world's demand for 594 years.[1] Like the deposits of Alsace those of Spain occur in marine sediments of Oligocene age; and it may be pointed out that the only other known deposits of potash outside of Germany, those of Kalusz in Galicia, Austrian Poland, also occur in Oligocene strata. If, from too strong focusing of the attention on the geology of the Stassfurt deposits the impression has become fixed that the Permian terranes are the most likely, or at best the only probable sources of potassium salts, a consideration of the discoveries in Alsace and of these in Spain shows that potassium deposits are not necessarily restricted to the Permian.

ADOLPH KNOPF.

[1] Förster, B., "Ergebnisse der Untersuchungen von Bohrproben aus den Tiefbohrungen im Tertiär des Oberelsass," *Mitt. Geol. Landesanstalt Elsass-Lothringen*, Vol. 7, p. 504, 1911.

SCIENTIFIC NOTES AND NEWS[1]

VANNOY H. MANNING has been appointed Director of the Bureau of Mines. For more than twenty years he has been engaged in technical and scientific work in the Department of the Interior. From 1885 to 1910, as civil engineer with the United States Geological Survey, he was engaged in topographic mapping in nearly every state of the union. When the Bureau of Mines was established in 1910, Manning was appointed to an administrative position in it, and on January 1, 1911, was made Assistant Director; he has been Acting Director of the Bureau in immediate charge of its work since January 1, 1914, at which time Doctor Holmes, on account of illness, had to relinquish active work.

HERBERT KYNASTON, director of the Geological Survey of the Union of South Africa, died at Pretoria, on June 28, aged forty-six years.

H. D. PALLISTER has resigned as assistant professor of mining at the School of Mines of the Pennsylvania State College to become professor of Geology and Mining at the School of Mines of the University of Texas, El Paso, Texas.

HOWLAND BANCROFT sailed from New Orleans on August 11 for South America, where he expects to spend the next few months in and about Bolivia examining various tin properties.

DR. J. A. UDDEN, geologist of the Bureau of Economic Geology in the University of Texas, has been appointed acting director of the bureau, the former director, Dr. Wm. B. Phillips, having resigned to become president of the Colorado School of Mines.

[1] Geologists, mining engineers and others interested in applied geology are invited to keep the editor informed of new investigations of mining districts or scientific studies undertaken by them, together with such other scientific and personal items as may come to their notice.

RALPH W. RICHARDS has just returned to Washington, D. C., after one and one-half year in Algeria with the Foreign Department of S. Pearson & Son, London.

PROFESSOR WALDEMAR LINDGREN has resigned his position as geologist in the U. S. Geological Survey.

PROFESSOR J. D. IRVING is examining a mining property at Butte.

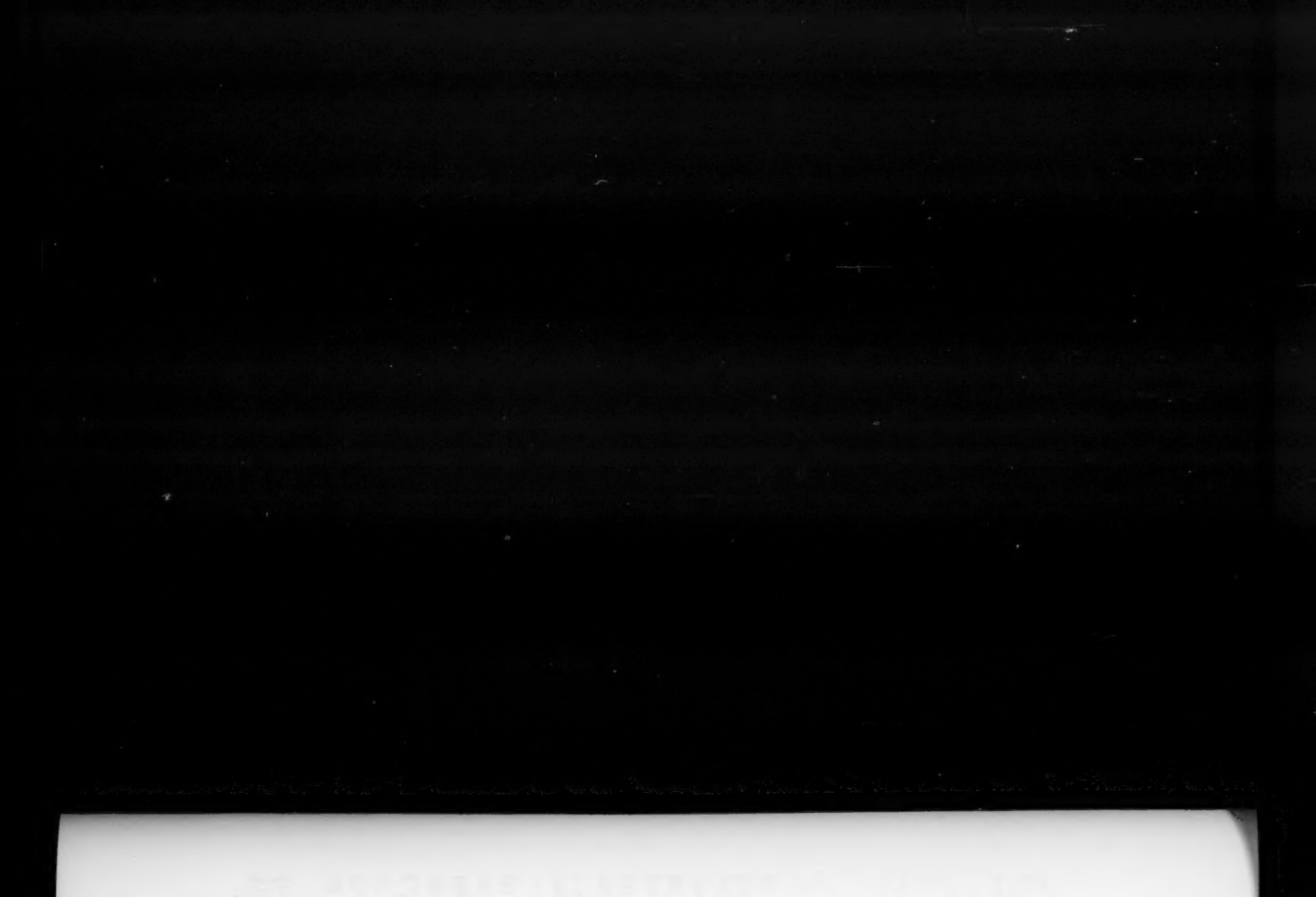
IN ORDER to urge mining law revision the Mining and Metallurgical Society of America has arranged for a meeting in Washington, December 16, 1915, at which meeting, not only this society, but all other organizations interested in the changes proposed might present such facts and arguments to the members of congress and other interested officials as would bring about some positive action by the government during the next session of congress. Mr. H. V. Winchell, Chairman of the Committee on mining law of the society, on February 15, 1915, presented to the council a progress report which was printed in the February bulletin, and which contained the suggestion upon which the action of the society is based.

THE SOUTHERN CALIFORNIA section of the American Institute of Mining Engineers announces an attractive program for its autumn and winter meetings. Among the subjects chosen for discussion are the following: December 14, "General Geology and Mining Conditions in Southern California;" February 1, 1916, "Petroleum, its Geology and Technology."

AMONG RECENT PUBLICATIONS of the U. S. Geological Survey we note Bulletins 611 to 614 comprising parts A to C of the "Guide Book of the Western United States" and entitled in order "The Northern Pacific Route," "The Overland Route," "The Santa Fe Route and the Shasta Route and the Coast Line." Too much praise can not be given to the Director for the initiative and to the several geologists for the splendid execution of this task. The Bulletins are sold at one dollar per copy in paper cover.

GEOLOGISTS will be interested in Bulletin 591, a new edition by Professor F. W. Clarke of the Analyses of rocks and minerals from the laboratory of the U. S. Geological Survey.

BULLETIN 72 of the Bureau of Mines gives the valuable results of an investigation on the "Occurrence of Explosive Gases in Coal Mines," by N. H. Darton.

AMONG the latest publications of the Geological Survey of Canada are the following memoirs: "The Artesian Wells of Montreal," by C. L. Cumming; "Coalfields of British Columbia," by D. B. Dowling; "A List of Canadian Mineral Occurrences," by Robert A. A. Johnston; "Geology of Cranbrook Map Area, British Columbia," by Stuart J. Schofield.

AMONG the papers presented at the recent San Francisco meeting of the Geological Society of America, we note the following: "Some Chemical Factors Affecting Secondary Sulphide Enrichment," by S. W. Young; "The Rôle of Colloidal Migration in Ore Deposits," by John D. Clark; "Some Examples of Progressive Change in the Mineral Composition of Copper Ore," by C. F. Tolman, Jr.; "Sericite, a Low Temperature Hydrothermal Mineral," by A. F. Rogers; "Examples of Successive Replacement of Earlier Sulphide Minerals by Later Sulphides at Butte, Montana," by J. C. Ray; and "Certain Structural Features in the Coal Fields of New Mexico," by Charles Kirk.